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Locating and Estimating Air Emissions from Sources of Benzene

Radian Corp., Research Triangle Park, NC

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16. ABSTRACT

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this to compile available information on sources and emissions of these substances. This document deals specifically with benzene. Its intended audience includes Federal, State and local air pollution personnel and others interested in locating potential emitters of benzene making gross estimates of air emissions therefrom.

This document presents information on (1) the types of sources that may emit benzene, (2) process variations and release points that may be expected within these sources, and (3) available emissions information indicating the potential for benzene release into the air from each operation.

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U.S. ENVIRONMENTAL PROTECTION AGENCY
Office Of Air And Radiation
Office Of Air Quality Planning And Standards
Research Triangle Park, North Carolina 27711

March 1988

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TABLE OF CONTENTS

Section Page

1 PURPOSE OF DOCUMENT 1

2 OVERVIEW OF DOCUMENT CONTENTS 3

3 BACKGROUND INFORMATION 5

Overview of Production and Use 7

References for Section 3 12

4 EMISSIONS FROM BENZENE PRODUCTION 14

Benzene Production 14

Process Description: Catalytic Reforming/ Separation 19

Emissions of Benzene from Catalytic Reforming/ Separation 22

Process Description: Toluene Dealkylation and Toluene Disproportionation 23

Emissions of Benzene from Toluene Dealkylation 23

Emissions of Benzene from Toluene Disproportionation 25

Process Description: Pyrolysis Gasoline 25

Benzene Emissions from Ethylene Plants and Benzene Recovery from Pyrolysis Gasoline 39

Process Description: Coke Oven Light Oil Distillation 43

Benzene Emissions from Coke By-product Plants 53

Process Description: Petroleum Refineries 62

Emissions of Benzene from Petroleum Refineries 73

References for Section 4 77

Section Page

5 EMISSIONS FROM INDUSTRIES USING BENZENE 79

Ethylbenzene Production 79

Process Description: Ethylbenzene and Styrene Production Using Benzene Alkylation and Ethylbenzene Dehydrogenation 83

Process Description: Ethylbenzene from Mixed Xylenes 85

Process Description: Styrene from Ethylbenzene Hydroperoxidation 86

Process Description: Styrene Production by an Isothermal Method 88

Benzene Emissions from Ethylbenzene and Styrene Production 90

Cyclohexane Production 95

Process Description: Benzene Hydrogenation 95

Benzene Emissions from Cyclohexane Production via Benzene Hydrogenation 98

Process Description: Separation of Petroleum Fractions 99

Benzene Emissions from Cyclohexane Production via Separation of Petroleum Fractions 102

Cumene Production 103

Benzene Emissions from Cumene Production 107

Phenol Production 108

Benzene Emissions from Phenol Production 112

Nitrobenzene Production 112

Process Descriptions 112

Benzene Emissions from Nitrobenzene Production 116

Aniline Production 120

Section Page

Benzene Emissions from Aniline Production 120

Chlorobenzene Production 123

Linear Alkylbenzene and Branched Alkylbenzene Production 128

Production of LAB Using the Chlorination Process 128

Benzene Emissions from LAB Production Using the Chlorination Process 132

Production of LAB Using the Olefin Process 134

Process Emissions from the LAB Olefin Process 136

Maleic Anhydride Production 138

Process Description 138

Gasoline Marketing 138

Benzene Emissions from Loading Marine Vessels 139

Benzene Emissions from Bulk Gasoline Plants, Bulk Gasoline Terminals and Service Stations 142

Control Technology for Gasoline Transfer 149

Control Technology for Gasoline Storage 153

Control Technology for Vehicle Refueling Emissions ... 153

Benzene Emissions from Motor Vehicles 155

Benzene Use as a Solvent 158

Benzene Emissions for Treatment, Storage, and Disposal Facilities (TSDF) 162

Benzene Emissions from Stationary Combustion Sources 162

References for Section 5 166

6 SAMPLING AND ANALYTICAL METHODS 169

Sampling and Analytical Procedures 171

Reference Method 21 - Determination of Volatile Organic Compound Leaks 171

Section | Page

Reference Method 18 - Measurement of Gaseous Organic Compound Emissions by Gas Chromatography 171

The Integrated Bag Sampling and Analytical Procedure 175

Protocol for the Collection and Analysis of Volatile POHCs Using VOST 180

Stainless Steel Canister Method - Urban Air Toxics Program 181

Sample Analysis 183

References for Section 6 186

Appendix A - DERIVATION OF EMISSION FACTORS A-1

A.1 Benzene Emissions from Ethylene Plants A-1

A.2 Derivation of Emission Factors for Fugitive Emissions from Chlorobenzene Production A-2

A.3 Derivation of Benzene Emission Factor for Exhaust Emission of Light Duty and Heavy Duty Trucks A-7

A.4 Benzene Emissions for Various Vehicle Test Types and Control Technologies A-8

References for Appendix A A-10

Appendix B - DATA ON POTENTIAL SOURCES OF BENZENE FROM THE AIR EMISSIONS SPECIES MANUAL (DRAFT REPORT) B-1

References for Appendix B B-7

LIST OF TABLES

Table Page

1 Physical and Chemical Properties of Benzene (C_6H_6) 6

2 Benzene Production Facilities 15

3 Ethylene Producers - Location and Capacity 28

4 Stream Designations for Figure 6, Production of Benzene from Pyrolysis Gasoline 32

5 Uncontrolled and Controlled Benzene Emission Factors for a Hypothetical Ethylene Plant 40

6 Coke Oven Batteries Currently Operating in the United States 44

7 Benzene Emission Factors for Furnace and Foundry Coke By-product Plants 57

8 Benzene Emission Factors for Equipment Leaks at Furnace and Foundry Coke By-product Plants 59

9 United States Refineries: Location by State and Capacities 63

10 Potential Sources of Benzene Emissions and Petroleum Refineries 74

11 Estimated Concentrations of Benzene in Nonmethane Hydrocarbon Fugitive Emissions for Selected Refining Processes 75

12 Emission Factors for Nonmethane Hydrocarbons and Estimated Benzene Fraction at Petroleum Refineries 76

13 United States Ethylbenzene and Styrene Producers, Location, and Capacity 81

14 Emission Factors for Ethylbenzene/Styrene Production via Alkylation and Dehydrogenation 91

15 United States Producers of Cyclohexane 96

16 Estimated Emission Factors for Benzene from Cyclohexane Production via Benzene Hydrogenation 100

Table		Page
17	United States Producers of Cumene and Annual Capacity	104
18	VOC Emissions and Weight Percent Benzene for Hypothetical Plant Producing Cumene by Process Using Aluminum Chloride Catalyst	109
19	United States Producers of Phenol, Their Locations and Capacities	110
20	United States Nitrobenzene Producers, Locations, and Capacity	113
21	Uncontrolled and Controlled Benzene Emission Factors for Hypothetical Nitrobenzene Production Plants	117
22	United States Producers of Aniline, Their Locations and Capacities	121
23	United States Producers of Mono-, Di-, and Trichlorobenzene	124
24	Benzene Emissions from a Hypothetical Plant Manufacturing Chlorobenzene Products	127
25	United States Producers of Alkylbenzene (Detergent Alkylates)	129
26	Benzene Emissions for a 90 Gg/Yr Hypothetical LAB Plant Using the Chlorination Process	133
27	Benzene Emissions for a 90 Gg/Yr Hypothetical LAB Plant Using the Olefin Process	137
28	Uncontrolled Volatile Organic Compound and Benzene Emissions from Loading Gasoline in Marine Vessels	141
29	Benzene Emission Factors for Gasoline Loading and Bulk Terminals and Bulk Plants	143
30	Benzene Emission Factors for Storage Losses at a Typical Gasoline Bulk Terminal	146
31	Uncontrolled Gasoline Vapor and Benzene Emissions from a Typical Bulk Plant	148
32	Uncontrolled Gasoline Vapor and Benzene Emissions from a Typical Service Station	150

Table | Page

33 Benzene Emissions Expressed as Percentage of Exhaust and Evaporative Emissions for Different Vehicle Classes 157

34 Industries and Products Possibly Using Benzene as a Solvent 159

35 United States Producers of Ethanol or Isopropanol 160

36 Summary of Organic Emission Factors for the Iron and Steel, Iron Foundry, and Ferroalloy Industries 165

A-1 Fugitive Emission Factors for Petroleum Refineries Used to Develop Factors for Chlorobenzene Production A-3

A-2 Benzene Emissions for Different Exhaust Emission Control Technologies A-9

B-1 Potential Sources of Benzene Emissions and Approximate Benzene Composition of the Emissions B-2

LIST OF FIGURES

Figure		Page
1	Production and Use Tree for Benzene	10
2	Universal Oil Products Platforming (Reforming) Process	20
3	Flow Diagram of a Glycol BTX Unit Process	21
4	Process Flow Diagram of a Toluene Dealkylation Unit	24
5	Toluene Disproportionation Process Flow Diagram (Tatoray Process)	26
6	Process Flow Diagram for Ethylene Production from Naphtha and/or Gas-Oil Feeds	30
7	Production of BTX by Hydrogenating Pyrolysis Gasoline	38
8	Coke Oven By-product Recovery, Representative Plant	49
9	Litol Process Flow Diagram	52
10	Process Flow Diagram for a Model Petroleum Refinery	72
11	Process Flow Diagram for Production of Styrene from Benzene and Ethylene by Dehydration of Ethylbenzene	84
12	Ethylbenzene Hydroperoxidation Process Block Diagram	87
13	Isothermal Processing of Styrene	89
14	Process Flow Diagram for Cyclohexane Production Using the Benzene Hydrogenation Process	97
15	Process Flow Diagram for Cyclohexane from Petroleum Fractions	101
16	Process for the Manufacture of Cumene Using Solid Phosphoric Acid Catalyst	105
17	Simplified Process Flow Diagram for Cumene Production Using Aluminum Chloride Catalyst	106
18	Flow Diagram for Manufacture of Phenol by the Cumene Peroxidation Process	111

Figure Page

19 Process Flow Diagram for Manufacture of Nitrobenzene 114

20 Flow Diagram for the Manufacture of Aniline 122

21 Monochlorobenzene and Dichlorobenzene by the Direct Chlorination of Benzene 125

22 Flow Diagram for LAB Chlorination Process Model Plant with Uncontrolled Emissions 131

23 Flow Diagram for LAB Olefin Process Model Plant 135

24 The Gasoline Marketing Distribution System in the United States 140

25 Bulk Plant Vapor Balance System 151

26 Service Station Vapor Balance System 152

27 Schematic Diagram of the Direct Interface Sampling System 174

28 Schematic Diagram of the Heated Box Required for the Dilution Interface Sampling Procedure 176

29 Schematic Diagram of the Integrated Bag Sampling System 177

30 Schematic Diagram of the Explosion Risk Area Gas Sampling System 178

31 Schematic Diagram of the Volatile Organic Sampling Train 182

32 Sampling Assembly for 24-Hour Urban Air Toxics Monitoring Program 184

SECTION 1

PURPOSE OF DOCUMENT

The Environmental Protection Agency, State, and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Unfortunately, very little information is available on the ambient air concentrations of these substances or on the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this that compiles available information on sources and emissions of these substances. Other documents in the series are listed below:

Substance	EPA Publication Number
Acrylonitrile	EPA-450/4-84-007a
Carbon Tetrachloride	EPA-450/4-84-007b
Chloroform	EPA-450/4-84-007c
Ethylene Dichloride	EPA-450/4-84-007d
Formaldehyde	EPA-450/4-84-007e
Nickel	EPA-450/4-84-007f
Chromium	EPA-450/4-84-007g
Manganese	EPA-450/4-84-007h
Phosgene	EPA-450/4-84-007i
Epichlorohydrin	EPA-450/4-84-007j
Vinylidene Chloride	EPA-450/4-84-007k
Ethylene Oxide	EPA-450/4-84-007l
Chlorobenzenes	EPA-450/4-84-007m
Polychlorinated Biphenyls (PCBs)	EPA-450/4-84-007n
Polycyclic Organic Matter (POM)	EPA-450/4-84-007p

This document deals specifically with benzene. Its intended audience includes Federal, State, and local air pollution personnel and others who are interested in locating potential emitters of benzene and making gross estimates of air emissions therefrom.

Because of the limited amounts of data available on some potential sources of benzene emissions, and since the configurations of many sources will not be the same as those described herein, this document is best used as a primer to inform air pollution personnel about (1) the types of sources that may emit benzene, (2) process variations and release points that may be expected within these sources, and (3) available emissions information indicating the potential for benzene to be released into the air from each operation.

The reader is strongly cautioned against using the emissions information contained in this document to try to develop an exact assessment of emissions from any particular facility. Since insufficient data are available to develop statistical estimates of the accuracy of these emission factors, no estimate can be made of the error that could result when these factors are used to calculate emissions from any given facility. It is possible, in some extreme cases, that orders-of-magnitude differences could result between actual and calculated emissions, depending on differences in source configurations, control equipment, and operating practices. Thus, in situations where an accurate assessment of benzene emissions is necessary, source-specific information should be obtained to confirm the existence of particular emitting operations, the types and effectiveness of control measures, and the impact of operating practices. A source test and/or material balance should be considered as the best means to determine air emissions directly from an operation.

SECTION 2

OVERVIEW OF DOCUMENT CONTENTS

As noted in Section 1, the purpose of this document is to assist Federal, State, and local air pollution agencies and others who are interested in locating potential air emitters of benzene and making gross estimates of air emissions therefrom. Because of the limited background data available on some potential sources of benzene, the information summarized in this document does not and should not be assumed to represent the source configuration or emissions associated with any particular facility.

This section provides an overview of the contents of this document. It briefly outlines the nature, extent, and format of the material presented in the remaining sections of this report.

Section 3 of this document provides a brief summary of the physical and chemical characteristics of benzene and an overview of its production and uses. This background section may be useful to someone who needs to develop a general perspective on the nature of benzene and how it is manufactured and consumed.

Section 4 of this document focuses on major industrial source categories that may discharge benzene air emissions. This section discusses the production of benzene. For each major production source category described in Section 4, example process descriptions and flow diagrams are given, potential emission points are identified, and available emission factor estimates are presented that show the potential for benzene emissions before and after controls employed by industry. Individual companies are named that are reported to be involved with the production of benzene, based primarily on trade publications.

Section 5 of this document concerns major source categories that use benzene as a feedstock and benzene in gasoline marketing. For each major production process, a description of the process is given along with process flow diagrams. Potential emission points are identified on the diagrams and emission factors are presented as available. Individual companies are listed that are reported to be using benzene as a feedstock.

The final section of this document summarizes available procedures for source sampling and analysis of benzene. Details are not prescribed nor is any EPA endorsement given to or implied for any of these sampling and analysis procedures. This document provides an overview of applicable sampling procedures, citing references for those interested in conducting source tests.

The appendix located at the end of this document presents derivations of benzene emission factors for the benzene production processes presented in Section 5. The development of these emission factors is discussed in detail for sources such as process vents, storage tank vents, liquid and solid waste streams, loading and handling, and leaks from process valves, pumps, compressors, and pressure relief valves.

This document does not contain any discussion of health or other environmental effects of benzene, nor does it include any discussion of ambient air levels.

Comments on the contents or usefulness of this document are welcomed, as is any information on process descriptions, operating practices, control measures, and emissions information that would enable EPA to improve its contents. All comments should be sent to:

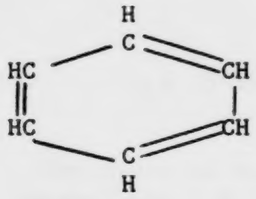
Chief, Pollutant Characterization Section (MD-15)
Noncriteria Pollutant Programs Branch
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

SECTION 3

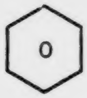
BACKGROUND INFORMATION

Benzene is a clear, colorless, aromatic hydrocarbon which has a characteristic sickly sweet odor. It is both volatile and flammable. Selected physical and chemical properties of benzene are presented in Table 1.[1,2]

Benzene contains 92.3 percent carbon and 7.7 percent hydrogen. The benzene molecule is represented by a hexagon formed by six sets of carbon and hydrogen atoms bonded together with alternating single and double bonds.



Benzene's chemical behavior indicates that the benzene molecule is more realistically represented as:



in which the carbon-to-carbon bonds are identical. The benzene molecule is the cornerstone for aromatic compounds, all of which contain one or more benzene rings.[3]

Benzene is nonpolar. It is relatively soluble in water and is miscible with polar solvents such as chloroform, acetone, alcohol, and carbon tetrachloride.

Due to its resonance properties, benzene is highly stable for an unsaturated hydrocarbon. But, it does react with other compounds primarily by substitution and, to a lesser degree, by addition. Some reactions also

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF BENZENE (C_6H_6)

Property	Value
Molecular weight	78.11
Melting point, °C	5.5
Boiling point, °C	80.100
Density at 20°C, g/mL	0.879
Vapor pressure at 25°C, KPa (mmHg)	12.7 (95.2)
Viscosity (absolute) at 20°C, mPa·S (=cP)	0.6468
Surface tension at 25°C, mN/m (=dyn/cm)	28.18
Flash point (closed cup), °C	-11.1
Heat of vaporization at 80.100°C, KJ/(Kg·mol) (Kcal/Kg·mol)	33.871 (8095)
Heat of combustion at constant pressure and 25°C (liquid C_6H_6 to liquid H_2O and gaseous CO_2), KJ/g (Kcal/g)	41.836 (9.999)
Solubility in water at 25°C, g/100g (ppm) water	0.180 (1800)
Solubility of water in benzene at 25°C, g/100g (ppm) benzene	0.05 (500)
Odor threshold (ppm)	0.875
Conversions	1 ppm = 319 mg/m^3 25°C 1 mg/liter = 313 ppm

Source: Reference 4.

occur which rupture or cleave to the molecule. Through all these types of reactions, many commercial chemicals are produced from benzene.[3]

Laboratory evaluations indicate that benzene is minimally reactive in the atmosphere, compared to the reactivity of other hydrocarbons. Reactivity can be determined by comparing the influence that different hydrocarbons have on the oxidation rate of nitric oxide (NO) to nitrogen dioxide (NO_2), or the relative degradation rate of various hydrocarbons when reacted with hydroxyl radicals (OH), atomic oxygen [$O(^3P)$] or ozone (O_3). For example, based on the NO oxidation test, the reactivity of benzene was determined to be one-tenth that of propylene and one-third that of n-hexane.[4]

Benzene shows long-term stability in the atmosphere.[3] Oxidation of benzene will occur only under extreme conditions, involving a catalyst or elevated temperature or pressure. Photolysis is possible only in the presence of sensitizers and is dependent on wavelength absorption. Benzene does not react with wavelengths greater than 275 nm.[3]

In laboratory evaluation, benzene was predicted to form phenols and ring cleavage products when reacted with hydroxide radicals (OH), and to form quinone and ring cleavage products when reacted with aromatic hydrogen.[5] Other products that are predicted to form from indirect reactions with benzene in the atmosphere include aldehydes, peroxides and epoxides. Photodegradation of NO_2 produces $O(^3P)$, which can react with atmospheric benzene to form phenols.[4]

OVERVIEW OF PRODUCTION AND USE

During the eighteenth century, benzene was discovered to be a component of oil, gas, coal tar, and coal gas. Around 1941, the commercial production of benzene from coal carbonization began in the United States for use primarily as feedstock in the chemical manufacturing industry.[1] Benzene is currently produced in the United States by 31 companies at 45 manufacturing facilities. The majority of benzene production facilities in the United

States are found in the vicinity of crude oil sources, predominantly located around the Texas and Louisiana gulf coast. They are also scattered through Oklahoma, Kansas, Illinois, and New Jersey.[7]

Domestic production in 1986 was estimated at a level of 8,709 million liters.[6] Benzene production levels are estimated to increase by approximately 2.3 percent per year through 1988. Exports of benzene are expected to remain steady at around one percent of the amount produced in the United States.[8]

Benzene is produced domestically by four major processes.[9] Approximately 50 percent of the benzene consumed in the United States is produced by the catalytic reforming/separation process. With this process, the naphtha portion of crude oil is mixed with hydrogen, heated, and sent through catalytic reactors.[10] The effluent enters a separator while the hydrogen is flashed off.[10] The resulting liquid is fractionated and the light ends (C_1-C_4) are split. Catalytic reformate, from which aromatics are extracted, is the product.[10]

Approximately 25 percent of the benzene produced in the United States is derived from liquid pyrolysis gasoline.[11] Pyrolysis gasoline is a by-product formed from the steam cracking of natural gas concentrates, heavy naphthas or gas oils to produce ethylene.[12]

Toluene dealkylation or toluene disproportionation processes account for another 20 percent of the United States production of benzene.[11] Toluene dealkylation produces benzene and methane from toluene or toluene-rich hydrocarbons through cracking processes using heat and hydrogen. The process may be either fixed bed catalyst or thermal. Toluene disproportionation produces benzene and xylenes from toluene using similar processes.[13]

The remainder of benzene produced in the United States is derived from coke oven light oil distillation at coke by-product plants.[9] Light oil is recovered from coke oven gas usually by continuous countercurrent absorption in a high boiling liquid from which it is stripped by steam distillation.[4] A light oil scrubber or spray tower removes the light oil from coke oven gas.[1] Benzene is recovered from the light oil by a number of processes, including fractionating to remove the lighter and heavier hydrocarbons, hydrogenation, and conventional distillation.

Figure 1 is a simplified production and use tree for benzene. Each major production process is shown, along with the percent of benzene derived from each process. The primary uses of benzene and the percentage for each use are also given in the figure. (The values given in Figure 1 total greater than 100 percent due to rounding.)

The major use of benzene is as a feedstock for chemical production, as in the manufacture of ethylbenzene (and styrene). In 1985, the manufacture of ethylbenzene (and styrene) accounted for 50 percent of benzene consumption.[9] Ethylbenzene is formed by reacting benzene with ethylene and propylene using a catalyst such as anhydrous aluminum chloride or solid phosphoric acid.[3] Styrene is the product of dehydrogenation of ethylbenzene.[4]

Twenty percent of the benzene supply is used to produce cumene.[11] Cumene is produced from benzene alkylation with propylene using solid phosphoric acid as a catalyst.[3] Cumene is oxidized to produce phenols and acetone.[11] Phenol is used to make resins for adhesive and plastic molding and caprolactum for nylon. Acetone is used to make solvents and plastics.[11]

Cyclohexane production accounts for fifteen percent of benzene use.[11] Cyclohexane is produced by reducing benzene hydrogenated vapors using a nickel catalyst at 200°C. Almost all of cyclohexane is used to make nylon or nylon intermediates.[11]

Chlorobenzene production accounts for 15 percent of benzene use. The halogenation of hot benzene with chlorine yields chlorobenzene. Monochlorobenzene and dichlorobenzene are produced by halogenation with chlorine using a molybdenum chloride catalyst.

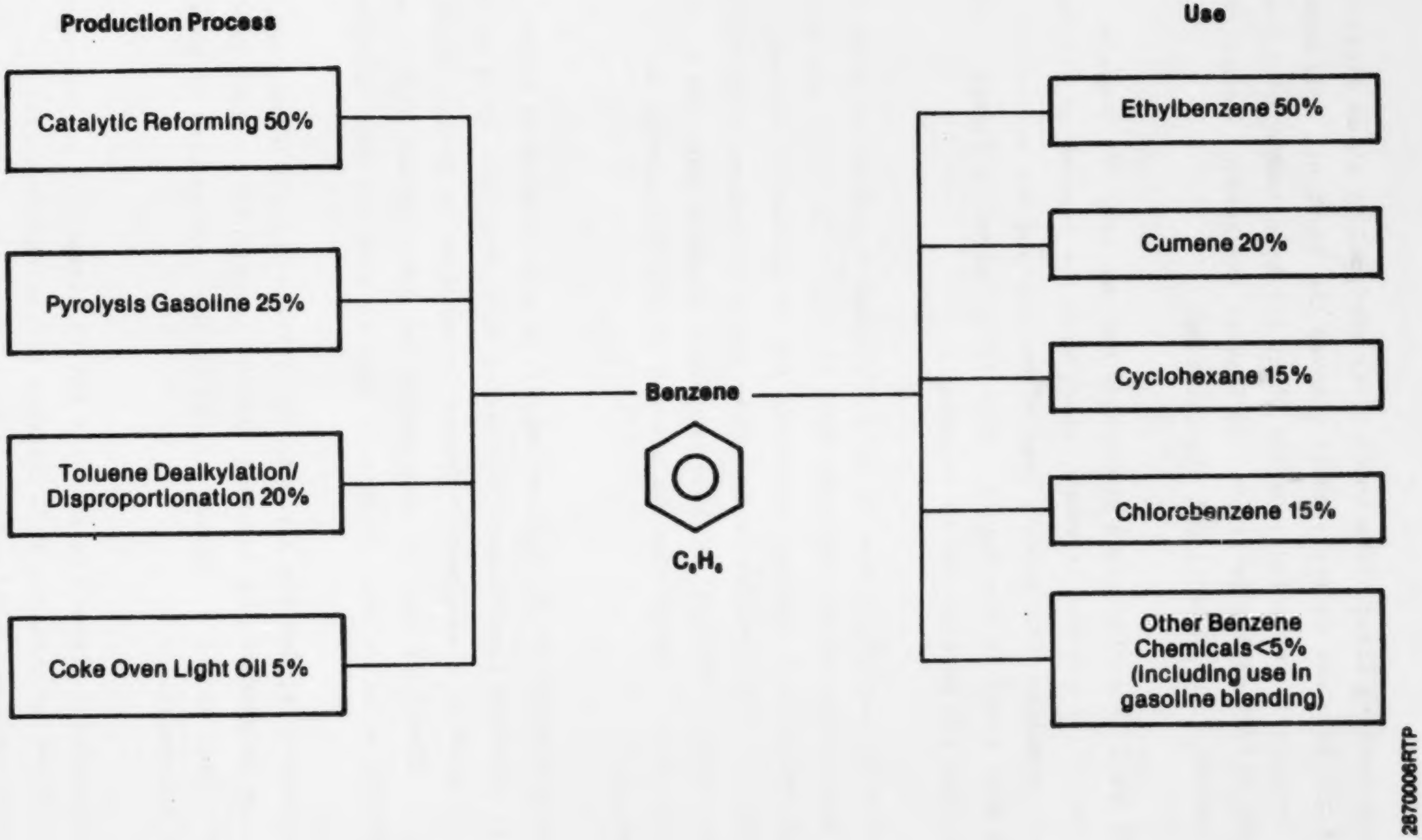

Production Process
Catalytic Reforming 50%
Pyrolysis Gasoline 25%
Toluene Dealkylation/ Disproportionation 20%
Coke Oven Light Oil 5%
Benzene
C_6H_6
Use
Ethylbenzene 50%
Cumene 20%
Cyclohexane 15%
Chlorobenzene 15%
Other Benzene Chemicals<5% (Including use in gasoline blending)
2870006RTP

Figure 1. Production and Use Tree for Benzene[1, 8, 9]

The production of nitrobenzene, from which aniline is made, accounts for five percent of benzene consumption.[11] Nitrobenzene is produced by the nitration of benzene with a concentrated acid mixture of nitric and sulfuric acid. Nitrobenzene is reduced to form aniline.[1] Aniline, in turn, is used to manufacture isocyanates for polyurethane foams, plastics, and dyes.[9]

Benzene has been used as a feedstock in the production of maleic anhydride.[4] However, in the United States, maleic anhydride is now produced using butane.[14] Monsanto Corporation has a 31.7 Mg capacity benzene-based plant which is on standby as of mid-1986.[14] A brief description of the benzene-based process is included in Section 4 of this document, for reference. Emissions of benzene associated with maleic anhydride manufacture are not included in this report.

The remainder of benzene production is consumed in the production of other chemicals. Other benzene-derived chemicals include alkylbenzene, bromobenzene, and diphenyl.

Benzene use as a solvent was once an important end use but is now on a rapid decline.[15] Due to the toxicity of the compound, benzene has been almost completely replaced with toluene or cyclohexane.[16]

Though much of the benzene consumed in the United States is used to manufacture chemicals, another important use of benzene is as a gasoline blending agent to enhance octane value and as a volume component. The concentration of benzene in refined gasoline depends on many variables such as gasoline grade, refinery location and processes, and crude source.[4] Laboratory evaluations of different gasoline blends indicate that typical benzene concentrations in gasoline are around 1.24 liquid volume percent.[4] The various sources of benzene emissions associated with motor vehicles and gasoline marketing are discussed in Section 5 of this report.

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12. U. S. Environmental Protection Agency. Organic Chemical Manufacturing. Volume 9: Selected Processes. Report 3. Ethylene. EPA-450/3-80-028d. Research Triangle Park, NC. 1980.

13. U. S. Environmental Protection Agency. Evaluation of Benzene Petroleum Process Operation. EPA-450/3-79-002. Research Triangle Park, NC. 1978.

14. Chemical Marketing Reporter. Chemical Profile. Maleic Anhydride. July 21, 1986.

15. Forrest, A. S. and G. E. Wilkins. Benzene: Solvent Usage and Waste Disposal Technical Memorandum. Prepared for R. G. Kellam, U. S. Environmental Protection Agency. Research Triangle Park, NC. 1983.

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SECTION 4

EMISSIONS FROM BENZENE PRODUCTION

Sources of atmospheric emissions of benzene related to its production are described in this section. Process flow diagrams are included as appropriate and the specific streams or vents in the figures are labeled to correspond to the discussion in the text. Emission factors for the production processes are presented when available and control technologies are described. More detailed descriptions and derivations of some of the emission factors are shown in Appendix A. It is advisable for the reader to contact specific sources in question to verify the nature of the process used, production volume, and control techniques in place before applying any of the emission factors presented in this report.

BENZENE PRODUCTION

Benzene is recovered from petroleum or coal through one of four processes. The vast majority of benzene is derived from petroleum sources through (1) catalytic reforming of naphtha (and solvent extraction), (2) dealkylation or disproportionation of toluene, or (3) separation of pyrolysis gasoline. The fourth process is distillation of coke oven light oil.[1] Almost half of all benzene is produced domestically by the catalytic reforming of naphtha. Pyrolysis gasoline from olefin steam-cracking plants accounts for about 25 percent of the benzene supply and toluene dealkylation accounts for about 20 percent.[2] Distillation of coke oven light oil generally accounts for only about 5 percent of all benzene produced.[1] Table 2 lists the producers of benzene in the United States (and territories), the annual production capacity, and the production process used.

Each of the four major production processes is described below. Specific emission sources are identified and available information on emissions of benzene is presented after each process description.

TABLE 2. BENZENE PRODUCTION FACILITIES[7]

Company Name	Location	Annual Capacity (Millions of Gallons)	Production Processes
Amerada Hess Corporation Hess Oil Virgin Islands Corporation, subsidiary	St. Croix, Virgin Islands	65	Catalytic reformate
American Hoechst Corporation Petrochemicals and Plastics Group Petrochemicals Division	Bayport, Texas	15[a]	Toluene; captive
American Petrofina, Incorporated Fina Oil and Chemical Company, subsidiary	Port Arthur, Texas	28	Toluene
		28	Catalytic reformate
Amoco Corporation Amoco Oil Company, subsidiary	Texas City, Texas	85	Catalytic reformate; partly captive
		30	Pyrolysis gasoline; partly captive
Aristech Chemical Corporation	Clairton, Pennsylvania	45	Coke-oven light oil
Ashland Oil, Incorporated Ashland Chemical Company, division Petrochemicals Division	Catlettsburg, Kentucky	55	Coke-oven light oil; partly captive
		2	Catalytic reformate; partly captive
Atlantic Richfield Company Lyondell Petrochemical Company, subsidiary	Channelview, Texas	72	Pyrolysis gasoline; captive
	Houston, Texas	38	Catalytic reformate
		15	Toluene
Bethlehem Steel Corporation Steel Group	Sparrows Point, Maryland	16	Coke-oven light oil
Chevron Corporation Chevron Chemical Company, subsidiary Aromatics and Derivatives Division	Philadelphia, Pennsylvania	17	Catalytic reformate; captive
		21	Toluene; captive
	Port Arthur, Texas	28	Catalytic reformate; partly captive
		40	Pyrolysis gasoline; partly captive
		40	Toluene; partly captive
The Coastal Corporation Coastal States Marketing, Incorporated, subsidiary	Corpus Christi, Texas	70[b]	Toluene

TABLE 2. BENZENE PRODUCTION FACILITIES[7] (Continued)

Company Name	Location	Annual Capacity (Millions of Gallons)	Production Processes
Corpus Christi Petrochemical Company	Corpus Christi, Texas	35	Pyrolysis gasoline; partly captive
		25	Toluene/xylenes fraction from pyrolysis gasoline; partly captive
Crown Central Petroleum Corporation Chemical Division	Pasadena, Texas	18	Toluene
		4	Catalytic reformate
Dow Chemical U.S.A.	Freeport, Texas	25	Pyrolysis gasoline; captive
		25	Toluene; captive
	Plaquemine, Louisiana	30	Pyrolysis gasoline; captive
		70	Toluene; captive
E.I. du Pont de Nemours and Company, Incorporated Petrochemicals Department Olefins and Aromatics Division	Chocolate Bayou, Texas	100[c]	Pyrolysis gasoline; partly captive
		40	Toluene; partly captive
Exxon Corporation Exxon Chemical Company, division Exxon Chemical Americas	Baton Rouge, Louisiana	42	Catalytic reformate
		37	Pyrolysis gasoline
	Baytown, Texas	90	Catalytic reformate; partly captive
		30	Pyrolysis gasoline; partly captive
Independent Refining Corporation	Winnie, Texas	4[b]	Catalytic reformate
Kerr-McGee Corporation Southwestern Refining Company, Incorporated, subsidiary	Corpus Christi, Texas	16	Catalytic reformate
Koch Industries, Incorporated Koch Refining Company, subsidiary	Corpus Christi, Texas	13	Catalytic reformate; captive
		28	Toluene; captive
		10	Xylene; captive
Mobil Corporation Mobil Oil Corporation Mobil Chemical Company, division Petrochemicals Division	Beaumont, Texas	40	Catalytic reformate
		10	Pyrolysis gasoline

TABLE 2. BENZENE PRODUCTION FACILITIES[7] (Continued)

Company Name	Location	Annual Capacity (Millions of Gallons)	Production Processes
Phillips Petroleum Company Phillips 66 Company, subsidiary Petrochemicals Division	Sweeny, Texas	10	Catalytic reformate; captive
		12	Pyrolysis gasoline; captive
Phillips Puerto Rico Core, Incorporated, subsidiary	Guayama, Puerto Rico	41	Catalytic reformate; captive
		82	Toluene; captive
Salomon, Incorporated Hill Chemical	Houston, Texas	5	Catalytic reformate
Shell Oil Company Shell Chemical Company, division	Deer Park, Texas	65	Catalytic reformate; partly captive
		75	Pyrolysis gasoline; partly captive
	Odessa, Texas	5	Catalytic reformate
	Wood River, Illinois	45	Catalytic reformate
Southland Corporation Chemical Division	Lake Charles, Louisiana	25	Catalytic reformate
The Standard Oil Company (Ohio) Sohio Oil Company	Alliance, Louisiana	18	Catalytic reformate; captive
		47	Toluene; captive
Sohio Chemical Company, subsidiary Chemicals Department	Lima, Ohio	35	Catalytic reformate
		50	Toluene
Sun Company, Incorporated Sun Refining and Marketing Company, Incorporated, subsidiary	Marcus Hook, Pennsylvania	20	Catalytic reformate
		13	Toluene
	Toledo, Ohio	16	Catalytic reformate
		48	Toluene
	Tulsa, Oklahoma	10	Catalytic reformate; captive
		17	Toluene; captive
Tenneco, Incorporated Tenneco Oil Processing and Marketing, division	Chalmette, Louisiana	15	Catalytic reformate
Texaco, Incorporated Texaco Chemical Company, subsidiary	Delaware City, Delaware	15	Catalytic reformate
	El Dorado, Kansas	13	Catalytic reformate; captive
	Port Arthur, Texas	30	Catalytic reformate; partly captive
		30	Pyrolysis gasoline; partly captive

TABLE 2. BENZENE PRODUCTION FACILITIES[7] (Continued)

Company Name	Location	Annual Capacity (Millions of Gallons)	Production Processes
Union Pacific Corporation			
Champlin Petroleum Company, subsidiary	Corpus Christi, Texas	42	Catalytic reformate; captive
USX Corporation			
Marathon Oil Company, subsidiary			
Marathon Petroleum Company, subsidiary	Texas City, Texas	7	Catalytic reformate
Unocal Corporation			
Union Oil Company of California, subsidiary	Beaumont, Texas	12	Catalytic reformate; captive
	Lemont, Illinois	10	Catalytic reformate
		7	Coke-oven light oil
TOTAL		2298	

[a] All production is tolled for Huntsman Chemical Corporation.

[b] Plant is on standby.

[c] Company's internal supply of pyrolysis gasoline can support only 40 million gallons of production.

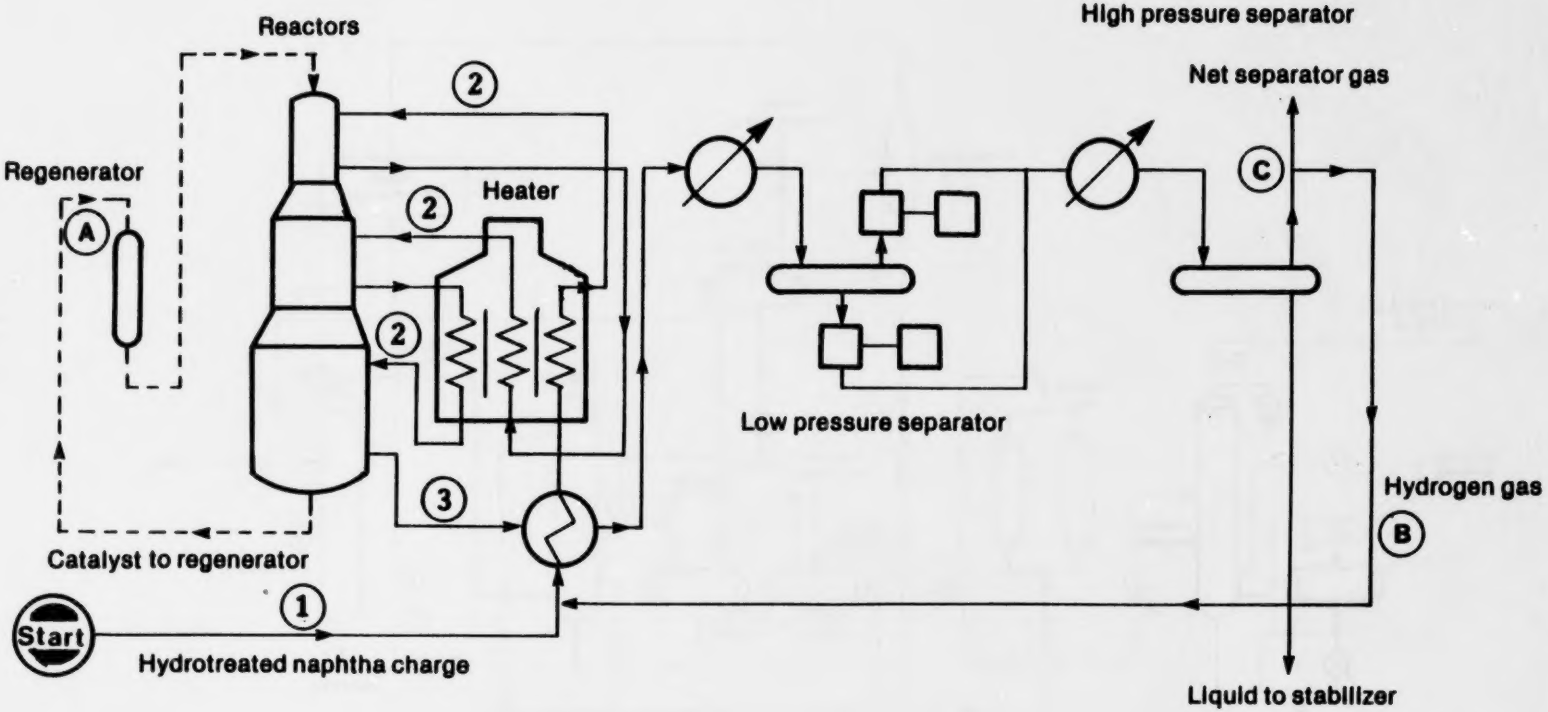
Note: This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of emissions from any given facility is a function of variables, such as throughput and control measures, and should be determined through direct contacts with plant personnel. Reference indicates that these data reflect changes made in production locations as of January 1987.

Process Description: Catalytic Reforming/Separation

Production of benzene by reforming/separation is associated with production of toluene and xylene (BTX plants).[3] Catalytic reforming is used to prepare high octane blending stocks for gasoline production and for producing aromatics as separate chemicals. The reforming process, shown in Figure 2, increases the quantity of aromatics in the naphtha fraction of the crude oil.[4] The naphtha fraction from crude oil is hydro-treated (mixed with hydrogen) (Stream 1), heated, and sent through catalytic reactors (Stream 2).[5] The catalyst, usually platinum or rhenium chloride, helps convert paraffins to aromatic compounds through dehydrocyclization, isomerication, and hydrocracking.[3,4] Effluent from the catalytic reactors is passed through a separator (Stream 3) where hydrogen is flashed off.[5] Hydrogen may be recycled to the reformer.[4] The liquid from the separator is fractionated and light ends are taken off. The product is the catalytic reformate, from which aromatics are extracted. The hydrogenation of naphthalenes is near 100 percent and from 0-70 percent of the paraffins are dehydrocyclized.[3]

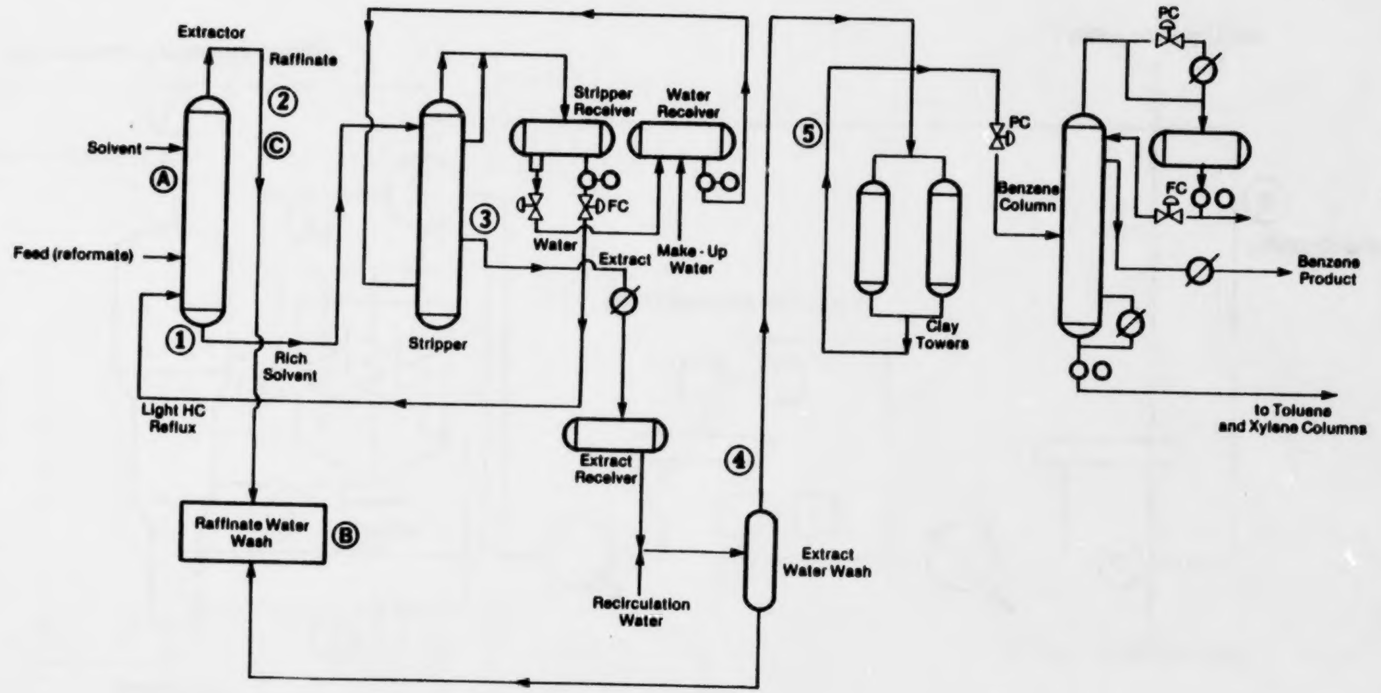
Several different solvents may be used to extract or separate benzene (and other aromatics) from the reformate. Glycols (tetraethylene glycol) and Sulfolane (1,1-tetrahydrothiophene dioxide) are most commonly used. The major difference in the two solvent extractions is that the glycol process requires one step to separate "rich solvent" in the stripper while the Sulfolane process requires two steps.[6]

In the glycol process (Figure 3), aromatics are separated from the reformate in the extractor. Solvent which contains the dissolved aromatics exits the bottom of the extractor (Stream 1). Raffinate leaves the top of the extractor (Stream 2) and is water washed and stored. In the stripper, the extract is steam-stripped and hydrocarbons are separated from the solvent. The extract, containing mostly aromatic hydrocarbons, is water washed to remove solvent (Stream 3). The extract is then heated and sent through clay towers to remove any olefins present (Stream 4). Then benzene, toluene, and xylene are separated by fractionation (Stream 5).[6]


Reactors
Regenerator
A
2
2
2
Heater
3
Catalyst to regenerator
Start
1
Hydrotreated naphtha charge
Low pressure separator
High pressure separator
Net separator gas
C
Hydrogen gas
B
Liquid to stabilizer

Note: The Stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 2. Universal Oil Products Platforming (Reforming) Process[3]


Extractor
Raffinate
②
Ⓒ
Solvent
Ⓐ
Feed (reformate)
①
Rich Solvent
Light HC Reflux
Raffinate Water Wash
Ⓑ
Stripper
③
Stripper Receiver
Water Receiver
FC
Water
Extract
Make - Up Water
Extract Receiver
Recirculation Water
④
Extract Water Wash
⑤
Clay Towers
PC
Benzene Column
PC
FC
Benzene Product
to Toluene and Xylene Columns

Note: Stream numbers on this figure correspond to the discussions in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 3. Flow Diagram of a Glycol BTX Unit Process[6]

The Sulfolane process is similar to the glycol process, but requires two steps to separate "rich solvent" (containing the aromatics) in the stripper. The fractionation of benzene, toluene, and xylene are the same as in the glycol process. Because the processes are similar, a detailed discussion of the Sulfolane process is not included in this report.

Emissions of Benzene from Catalytic Reforming/Separation

A literature search and review of materials in the docket (A-79-27) for some NESHAP efforts on benzene revealed no source-specific emission factors or emissions estimates for benzene from catalytic reforming/separation. However, some descriptive data were found, indicating that benzene may be emitted from the catalytic reforming process during catalyst regeneration or replacement, during recycling of hydrogen gas to the reformer, and from the light gases taken from the separator. These potential emission points are labeled as A, B, and C, respectively, on Figure 2.

One general estimate of the amount of benzene emitted by catalytic reforming has been reported in the literature. Walker (1976) estimated that 1 percent of total benzene produced by catalytic reforming was emitted.[4]

Benzene may be emitted from separation solvent regeneration, raffinate wash water, and raffinate in association with the separation processes following catalytic reforming. These potential sources are shown as A, B, and C, respectively, in Figure 3. However, no specific data were found showing emission factors or estimates for benzene emissions from these potential sources. One discussion of the Sulfolane process indicated 99.9 percent recovery of benzene was not unusual. Therefore, 0.1 percent of the benzene recovered may be a rough general estimate of the benzene emissions from separation processes.[4]

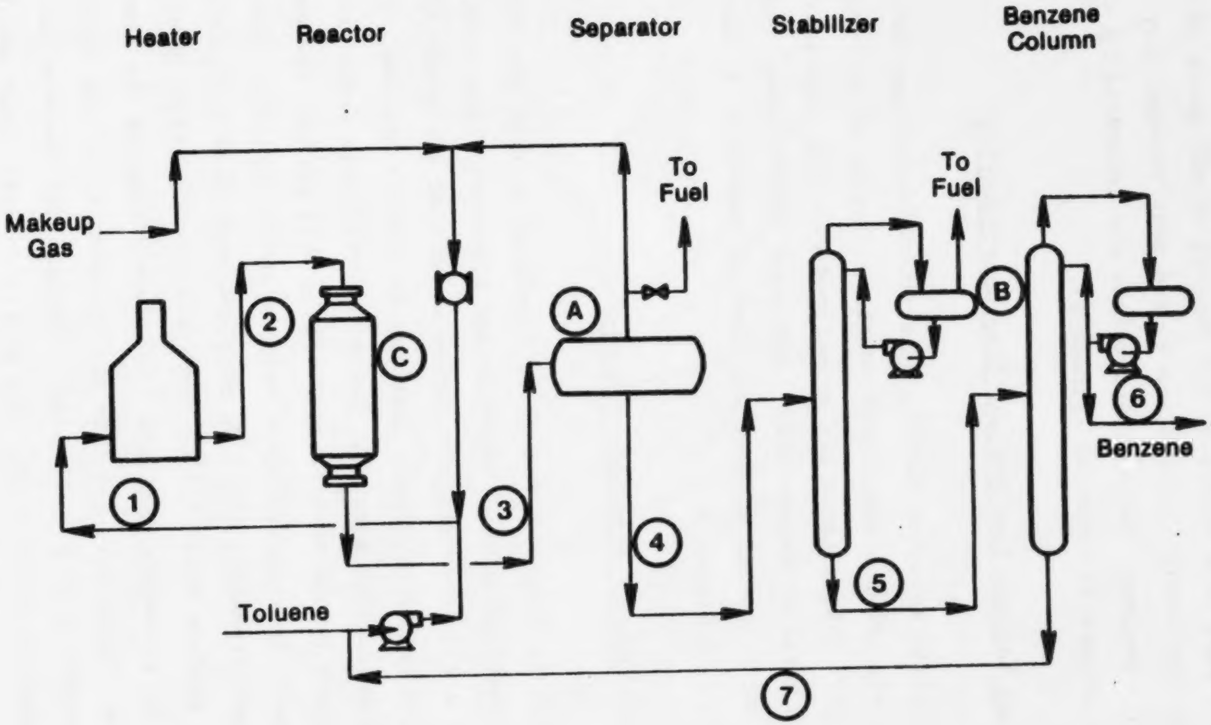
Process Description: Toluene Dealkylation and Toluene Disproportionation

Benzene may also be produced from toluene through dealkylation or disproportionation. Since there are now requirements for lower lead levels in gasoline, it may be more advantageous for some producers to use the toluene from reforming in gasoline blending (to raise octane) instead of in the production of benzene.[3] If benzene prices rise high enough, dealkylation of toluene may become more economically advantageous. Similarly, the price of xylene often drives the use of toluene disproportionation.

Dealkylation of toluene can be accomplished through thermal or catalytic processes.[6] The total dealkylation capacity is almost evenly split between the two methods.[3] As shown in Figure 4, pure toluene or toluene mixed with other aromatics or paraffins is heated (Stream 1) and is charged to the reactor (Stream 2) in the presence of excess hydrogen. Toluene reacts with the hydrogen to yield benzene and methane. The benzene may be separated from methane in a low pressure separator (Stream 3) by flashing off the methane-containing gas.[6] The product is then stabilized (Stream 4) and benzene is recovered by distillation (Stream 5).[3] The product is then sent to storage (Stream 6). Unreacted toluene and some heavy by-products are recycled (Stream 7). About 70-85 percent conversion of toluene to benzene is accomplished per pass through the system and the ultimate yield is 95 percent of the theoretical yield.[3]

Emissions of Benzene from Toluene Dealkylation

No source-specific emission factors were found concerning emissions of benzene from its production through dealkylation or disproportionation of toluene. Potential sources of benzene emissions from the dealkylation process include the separation of benzene and methane, distillation, and catalyst regeneration.[4] These potential sources are shown as points A, B, and C, respectively, in Figure 4.


Heater
Reactor
Separator
Stabilizer
Benzene Column
Makeup Gas
To Fuel
To Fuel
Toluene
Benzene
1
2
3
4
5
6
7
A
B
C

Note: Stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 4. Process Flow Diagram of a Toluene Dealkylation Unit[3,6]

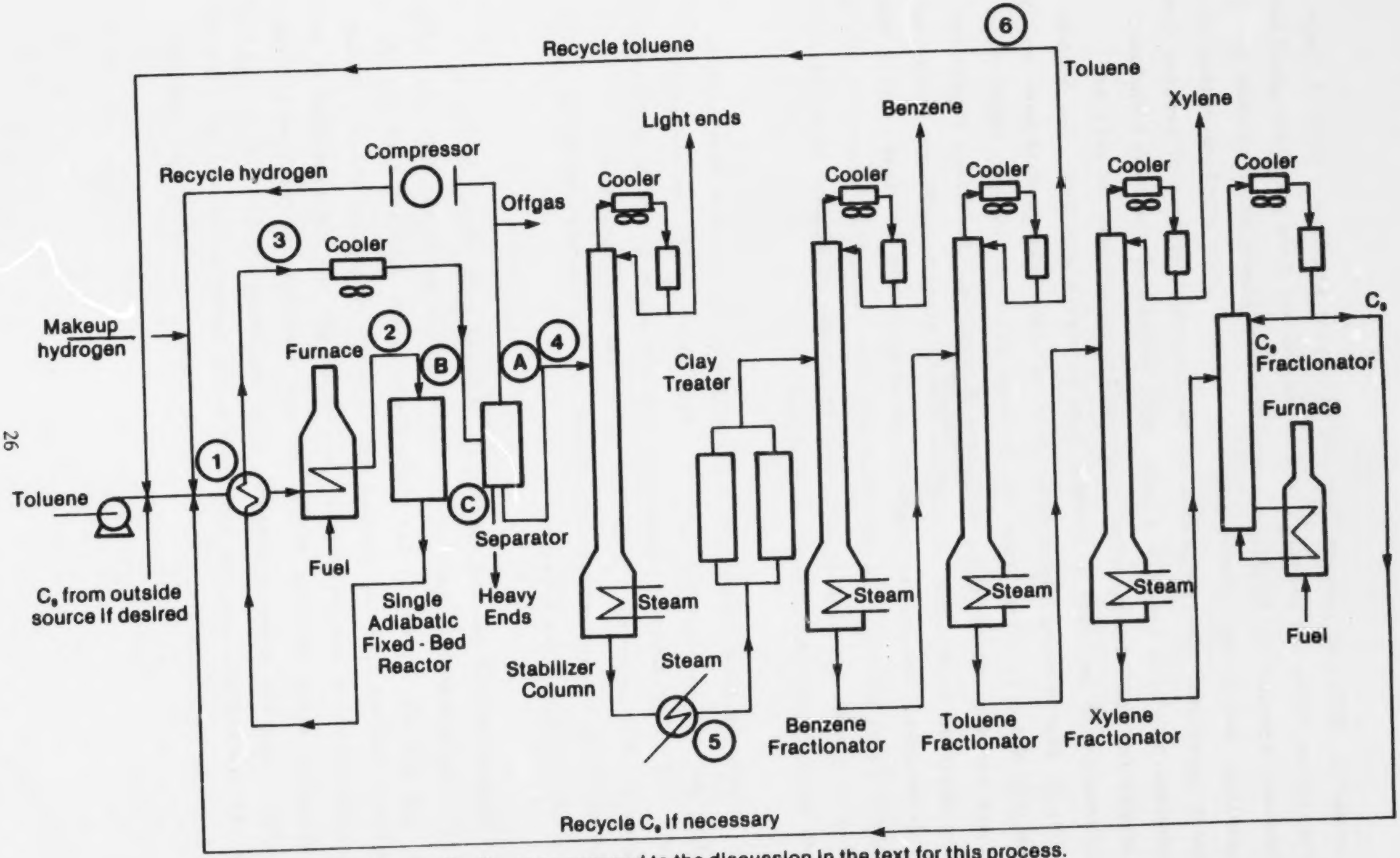
Toluene disproportionation produces benzene and xylenes from toluene by catalytic reaction. As shown in Figure 5, the basic process is similar to toluene dealkylation, but can occur under less severe conditions. Toluene is heated (Stream 1) and sent to the reactor (Stream 2). The reacted material is sent to a separator for removal of off gases (Stream 3). The product is then stabilized (Stream 4) and sent through clay towers (Stream 5). Benzene, toluene, and xylene are recovered by distillation and unreacted toluene is recycled (Stream 6).

Emissions of Benzene from Toluene Disproportionation

No specific emission factors were found for benzene emissions from its production via toluene disproportionation. Potential sources of benzene emissions from this process are associated with the separation of benzene and xylene, catalyst regeneration, and heavy hydrocarbons that do not break down.[4] These potential sources are shown as points A, B, and C, respectively, in Figure 5.

Process Description: Pyrolysis Gasoline

Ethylene is produced through pyrolysis of natural gas concentrates or petroleum fractions such as naphthas and atmospheric gas oils.[9] Pyrolysis gasoline is a liquid by-product formed as part of the steam cracking process. The liquid pyrolysis gasoline is rich in benzene. Ethylene plants of the same production capacity, but using different feedstocks (ethane/propane versus naphthas/gas oils), will produce different amounts of pyrolysis gasoline with different benzene concentrations. For example, an ethylene plant producing 453.5 Gg ethylene/year (1 billion pounds) from ethane will produce about 7.3 Gg pyrolysis gasoline with about 3.4 Gg benzene in the pyrolysis gasoline.[9] A plant producing the same amount of ethylene from atmospheric gas oils will produce about 342 Gg of pyrolysis gasoline containing 96.8 Gg benzene.[9] Because the benzene content of pyrolysis gasoline can be high, some plants recover motor gasoline,


Recycle toluene
⑥
Toluene
Light ends
Benzene
Xylene
Compressor
Recycle hydrogen
Offgas
Cooler
Cooler
Cooler
Cooler
Cooler
Cooler
③
Makeup hydrogen
②
Furnace
Ⓑ
Ⓐ
④
C_9
Clay Treater
C_9 Fractionator
Furnace
①
Toluene
Ⓒ
Separator
Fuel
C_9 from outside source if desired
Single Adiabatic Fixed - Bed Reactor
Heavy Ends
Steam
Steam
Steam
Steam
Steam
Fuel
Stabilizer Column
Steam
⑤
Benzene Fractionator
Toluene Fractionator
Xylene Fractionator
Recycle C_9 if necessary

Note: Stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5. Toluene Disproportionation Process Flow Diagram (Tatoray Process)[8]

aromatics (BTX), or benzene from the pyrolysis gasoline. Table 2 lists facilities which are reported to recover benzene from pyrolysis gasoline. However, benzene can be emitted from ethylene plants which produce pyrolysis gasoline, but do not recover benzene. Table 3 lists ethylene producers and their locations. To locate most of the potential sources of benzene from ethylene/pyrolysis gasoline plants, this section of the report includes information and ethylene/pyrolysis gasoline production, as well as information on recovery of benzene from pyrolysis gasoline. But because ethylene plants using naphthas/gas oils as feedstocks produce more pyrolysis gasoline and more often treat the gasoline prior to storage, these types of plants are emphasized in the following discussion. Reference 9 provides more detailed information on ethylene plants using natural gas concentrates as feedstocks. In general, natural gas-using plants are less complex than naphtha-using plants. The potential emission sources of benzene at the two types of plants are similar with smaller amounts of benzene being emitted from natural gas concentrate-using plants.

A process flow diagram for a plant producing ethylene from naphtha and/or gas oil is shown in Figure 6. Many older facilities use larger numbers of compressors (in parallel) than are shown in the flow diagrams in Figure 6. For reference, Table 4 lists stream descriptions and corresponding stream numbers from Figure 6. The description of the process is taken entirely from Reference 9.

Naphtha and/or gas oil (Stream 1), diluted with steam, is fed in parallel to a number of gas- or oil-fired tubular pyrolysis furnaces. The fuel gas and oil (Stream 2) for these furnaces are supplied from gas and oil fractions removed from the cracked gas in later separation steps. Ethane and propane, which are present in the cracked gas and are separated in later distillation steps (Streams 35 and 38), are combined and recycled (Stream 3) through a separate cracking furnace. The resulting cracked gas is combined with the cracked gas from the naphtha/gas-oil furnaces (Stream 5). The flue gas from the pyrolysis furnaces is vented (Vent A on Figure 6). During

TABLE 3. ETHYLENE PRODUCERS - LOCATION AND CAPACITY[7]

Producer	Location	Annual Capacity (Millions of Pounds)	Notes
Allied Corporation/BASF Wyandotte Corporation/ Borg-Warner Corporation	Geismar, Louisiana	740	Captive
Amoco Corporation Amoco Chemicals Company, subsidiary	Chocolate Bayou, Texas	2,075	Partly captive
Aristech Chemical Corporation	Houston, Texas	500	No captive use
Atlantic Richfield Company Lyondell Petrochemical Company, subsidiary	Channelview, Texas[a]	2,800	Some captive; mostly merchant
Chevron Corporation Chevron Chemical Company, subsidiary Olefins and Derivatives Division	Cedar Bayou, Texas	1,200	Partly captive
	Port Arthur, Texas[a]	950	Partly captive
Corpus Christi Petrochemical Company	Corpus Christi, Texas[a]	1,200	Some merchant; captive use for ICI and Soltex
Dow Chemical U.S.A.	Freeport, Texas[a]	1,850	Mostly captive
	Plaquemine, Louisiana	1,934	Captive
E. I. duPont de Nemours and Company, Inc. Petrochemicals Department Olefins and Aromatics Division	Chocolate Bayou, Texas[a]	990	Mostly merchant
	Orange, Texas	925	Mostly captive
Eastman Kodak Company Eastman Chemical Products, Inc., subsidiary Texas Eastman Company	Longview, Texas	1,340	Captive
El Paso Products Company	Odessa, Texas	520	Mostly captive
Exxon Corporation Exxon Chemical Company, division Exxon Chemical Americas	Baton Rouge, Louisiana	1,400	Partly captive
	Baytown, Texas[a]	1,400	Some captive use at Mont Belvieu, Texas
The BF Goodrich Company BF Goodrich Chemical Group	Calvert City, Kentucky	365	Captive
Koch Industries, Inc. Koch Refining Company, subsidiary	Corpus Christi, Texas	25	Captive

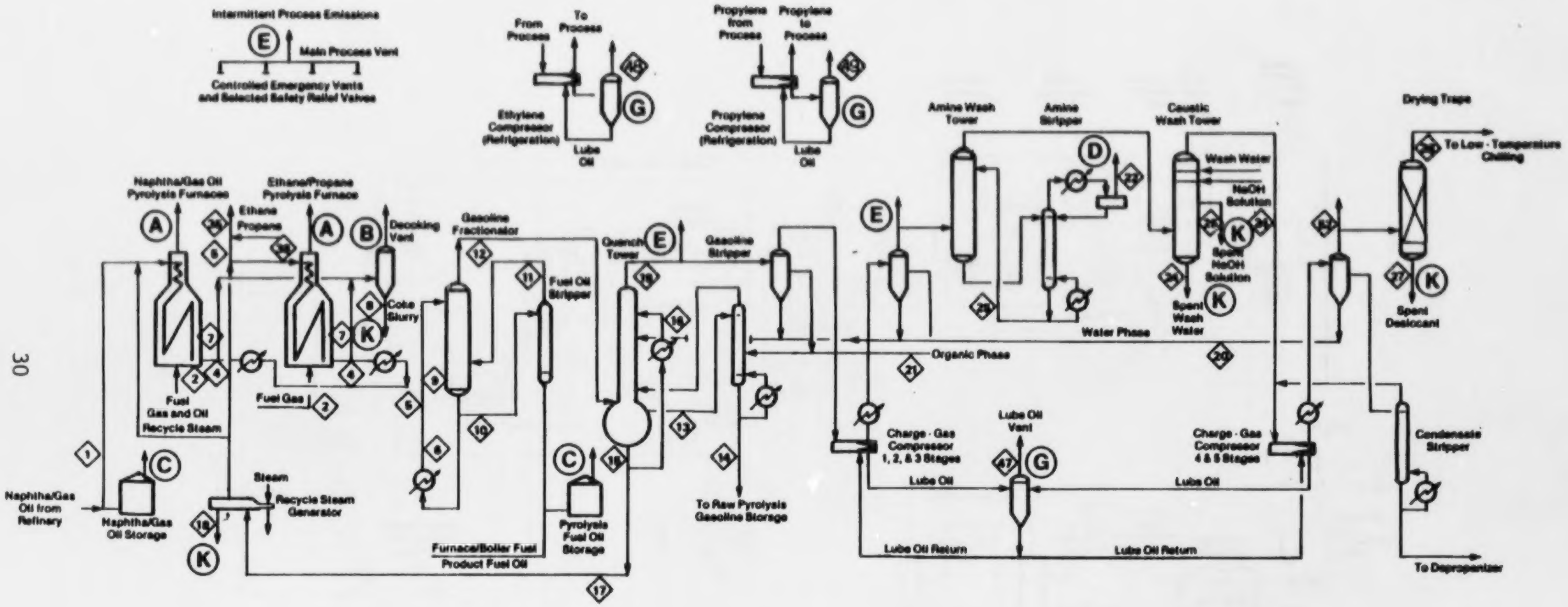
TABLE 3. ETHYLENE PRODUCERS - LOCATION AND CAPACITY[7] (Continued)

Producer	Location	Annual Capacity (Millions of Pounds)	Notes
Mobil Corporation Mobil Oil Corporation Mobil Chemical Company, division Petrochemicals Division	Beaumont, Texas[a]	1,050	Partly captive
National Distillers and Chemical Corporation Chemicals Division U. S. Industrial Chemicals Company, division	Clinton, Iowa	800	Captive
	Morris, Illinois	940	Captive
	Tuscola, Illinois	400	Captive
Phillips Petroleum Company Phillips 66 Company, subsidiary Petrochemicals Division	Sweeny, Texas[a]	2,520	Partly captive
Shell Oil Company Shell Chemical Company, division	Deer Park, Texas[a]	1,790	Partly captive
	Norco, Louisiana	2,240	Partly captive
SunOlin Chemical Company	Claymont, Delaware	225	Partly captive
Texaco, Inc. Texaco Chemical Company, subsidiary	Port Arthur, Texas[a]	1,050	Some captive use at Port Neches
	Port Neches, Texas	375[b]	Mostly captive
Union Carbide Corporation Ethylene Oxide/Glycol Division	Seadrift, Texas	825	Captive
	Taft, Louisiana[a]	725	Captive
	Texas City, Texas	1,250	Captive
Vista Chemical Company	Lake Charles, Louisiana	650	Mostly captive
TOTAL		35,609	

[a] Listed by Reference 7 as producing benzene from pyrolysis gasoline.

[b] On standby.

Note: This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of benzene emissions from any given facility is a function of variables, such as throughput and control measures, and should be determined through direct contacts with plant personnel. Data represent producers, locations, and capacities as of January 1987.


Intermittent Process Emissions
E
Main Process Vent
Controlled Emergency Vents and Selected Safety Relief Valves
From Process
To Process
Ethylene Compressor (Refrigeration)
Lube Oil
G
Propylene from Process
Propylene to Process
Propylene Compressor (Refrigeration)
Lube Oil
G
Naphtha/Gas Oil Pyrolysis Furnaces
A
Ethane Propane
Ethane/Propane Pyrolysis Furnace
A
B
Decoking Vent
Coke Slurry
K
Gasoline Fractionator
Fuel Oil Stripper
Quench Tower
E
Gasoline Stripper
Fuel Gas and Oil Recycle Steam
Fuel Gas
Naphtha/Gas Oil from Refinery
C
Naphtha/Gas Oil Storage
Steam
Recycle Steam Generator
K
Furnace/Boiler Fuel
Product Fuel Oil
C
Pyrolysis Fuel Oil Storage
To Raw Pyrolysis Gasoline Storage
1
2
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
21
22
23
24
25
26
27
28
29
30
47
E
Amine Wash Tower
Amine Stripper
D
Caustic Wash Tower
Wash Water
NaOH Solution
K
Spent NaOH Solution
Spent Wash Water
K
Water Phase
Organic Phase
Drying Traps
To Low - Temperature Chilling
Spent Desiccant
K
Charge - Gas Compressor 1, 2, & 3 Stages
Lube Oil Vent
G
Lube Oil
Lube Oil Return
Charge - Gas Compressor 4 & 5 Stages
Lube Oil
Lube Oil Return
Condensate Stripper
To Depropanizer

Note: The Stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions (see text).

Figure 6. Process Flow Diagram for Ethylene Production from Naphtha and/or Gas-Oil Feeds[9]

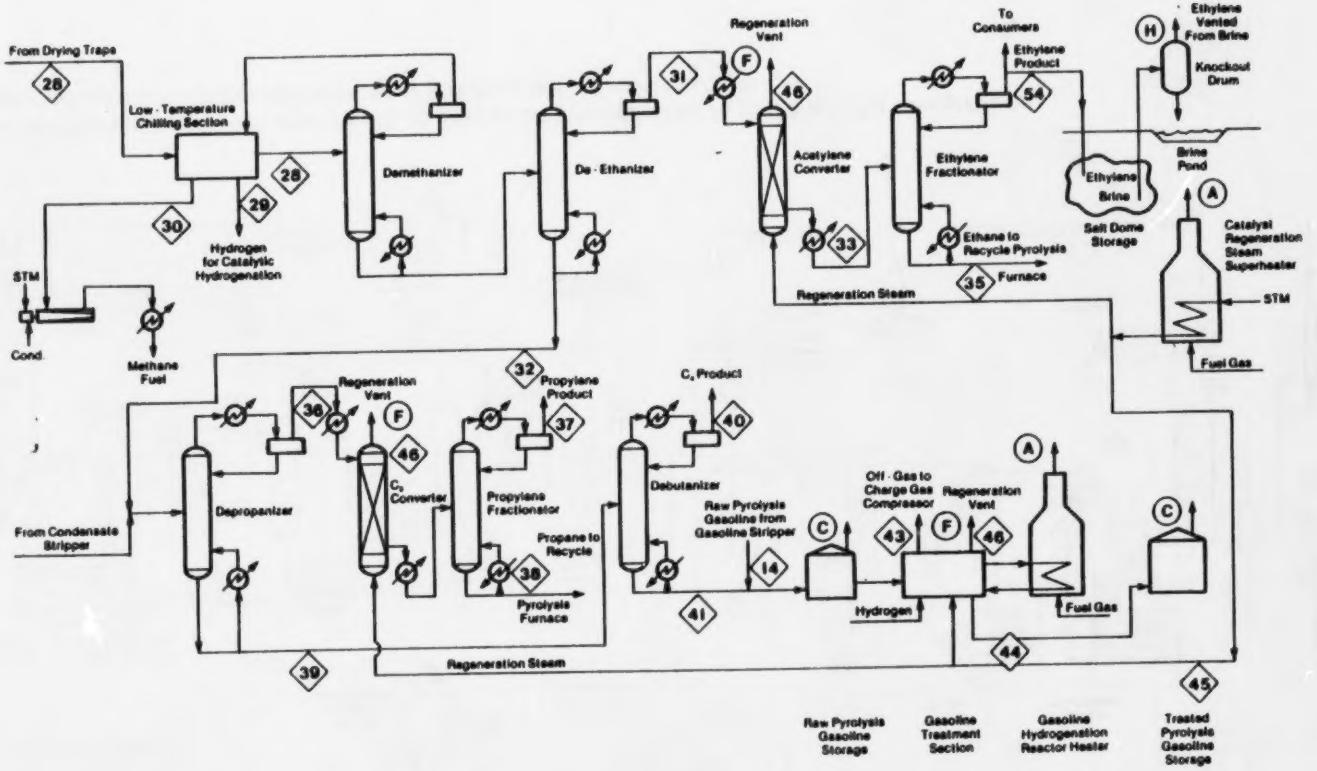

From Drying Traps
28
Low - Temperature Chilling Section
28
29
30
Hydrogen for Catalytic Hydrogenation
STM
Cond.
Methane Fuel
Demethanizer
De - Ethanizer
31
F
Regeneration Vent
46
Acetylene Converter
33
Regeneration Steam
Ethylene Fractionator
To Consumers
Ethylene Product
54
Ethane to Recycle Pyrolysis Furnace
35
H
Ethylene Vented From Brine
Knockout Drum
Brine Pond
Ethylene Brine
Salt Dome Storage
A
Catalyst Regeneration Steam Superheater
STM
Fuel Gas
32
From Condensate Stripper
Depropanizer
36
Regeneration Vent
F
46
C_3 Converter
Propylene Product
37
Propylene Fractionator
38
Propane to Recycle
Pyrolysis Furnace
39
Regeneration Steam
C_4 Product
40
Debutanizer
41
Raw Pyrolysis Gasoline from Gasoline Stripper
14
C
Off - Gas to Charge Gas Compressor
43
F
Regeneration Vent
46
Hydrogen
A
Fuel Gas
44
C
45
Raw Pyrolysis Gasoline Storage
Gasoline Treatment Section
Gasoline Hydrogenation Reactor Heater
Treated Pyrolysis Gasoline Storage

Figure 6. Process Flow Diagram for Ethylene Production from Naphtha and/or Gas-Oil Feeds[9] (Continued)

TABLE 4. STREAM DESIGNATIONS FOR FIGURE 6, PRODUCTION OF BENZENE FROM PYROLYSIS GASOLINE

Stream Number	Stream Description
1	Naphtha or gas oil feed
2	Fuel gas and oil
3	Ethane/propane recycle stream
4	Cracked gas
5	Cracked gas
6	Gasoline fractionator
7	Furnace exhaust
8	Slurry of collected particles
9	Quenched cracked gas
10	Surplus fuel oil
11	Light fractions
12	Overheads from gasoline fractionator
13	Condensed organic phase
14	Raw pyrolysis gasoline intermediate storage
15	Quench tower
16	Heat exchangers
17	Surplus water
18	Recycle steam generator blowdown
19	Overheads from quench tower
20	Water
21	Organic fractions
22	Acid gas
23	Diethanolamine (DEA)
24	Liquid waste stream
25	Liquid waste stream
26	Process gas stream
27	Solid waste stream

TABLE 4. STREAM DESIGNATIONS FOR FIGURE 6, PRODUCTION OF BENZENE FROM PYROLYSIS GASOLINE (Continued)

Stream Number	Stream Description
28	Process gas
29	Hydrogen rich stream from demethanizer
30	Methane rich stream from demethanizer
31	C_2 components from de-ethanizer
32	C_3 and heavier components from de-ethanizer
33	Acetylene convertor
34	Overheads from ethylene fractionator
35	Ethane recycle pyrolysis furnace
36	Overheads from depropanizer
37	Propylene (purified)
38	Propane recycle pyrolysis furnace
39	C_4 and heavier components to debutanizer
40	Overheads from debutanizer
41	C_5 and heavier components from debutanizer
42	Combined C_5 components and gasoline stripper bottoms fraction
43	Light ends to cracked gas compressor
44	C_5 and heavier components
45	Superheated stream
46	Stream and hydrocarbons
47	Compressor
48	Refrigeration compressor
49	Refrigeration compressor

operation, coke accumulates on the inside walls of the reactor coils, and each furnace must be periodically taken out of service for removal of the accumulated coke. Normally, one furnace is out of service for decoking at all times. Decoking is accomplished by passing steam and air through the coil while the furnace is maintained at an elevated temperature, effectively burning the carbon out of the coil. While a furnace is being decoked, the exhaust is diverted (Stream 7) to an emission control device (Vent B) whose main function is to reduce particulate emissions. The collected particles are removed as a slurry (Stream 8). The cracked gas (Stream 4) leaving the pyrolysis furnaces is rapidly cooled (quenched) to 250-300°C by passing it through transfer-line exchangers, which end pyrolysis and simultaneously generate steam. The streams from the transfer-line exchangers (Stream 5) are combined and further quenched by the injection of recycled pyrolysis fuel oil from the gasoline fractionator (Stream 6).

The quenched cracked gas (Stream 9) passes to the gasoline fractionator, where pyrolysis fuel oil is separated. Most of the fuel oil passes through water-cooled heat exchangers and is recycled (Stream 6) to the preceding oil-quenching operation. The surplus fuel oil (Stream 10), equivalent to the quantity initially present in the cracked gas, passes first to the fuel oil stripper, where light fractions are removed, and then to fuel oil storage. The light fractions (Stream 11) removed in the fuel oil stripper are recycled to the gasoline fractionator. The gasoline fractionator temperatures are well above the vaporization temperature of water, and the contained water remains as superheated steam, with the overhead stream containing the lighter cracked-gas components.

The overhead stream from the gasoline fractionator (Stream 12) passes to the quench tower, where the temperature is further reduced, condensing most of the water and part of the C_5 and heavier compounds. The condensed organic phase (Stream 13) is stripped of the lighter components in the gasoline stripper and is passed to raw pyrolysis gasoline intermediate storage (Stream 14). Most of the water phase, which is saturated with organics, is separated in the quench tower (Stream 15), passed through water-cooled heat exchangers (Stream 16), and then recycled to the quench tower to provide the necessary cooling. The surplus water (Stream 17), approximately equivalent to the quantity of steam injected with the pyrolysis furnace feed, passes to the dilution steam generator, where it is vaporized and recycled as steam to the pyrolysis furnaces. Blowdown from the recycle steam generator is removed as a wastewater stream (Stream 18).

The overhead stream from the quench tower (Stream 19) passes to a centrifugal charge-gas compressor (first three stages), where it is compressed. Water (Stream 20) and organic fractions (Stream 21) condensed during compression and cooling are recycled to the quench tower and gasoline stripper.

Lubricating oil (seal oil) discharged from the charge-gas compressor is stripped of volatile organics in a separator pot before the oil is recirculated. The organic vapor is vented to the atmosphere (Vent G). Similar separator pots separate volatile organics from lubricating oil from both the ethylene and propylene refrigeration compressors (Streams 48 and 49).

Following compression, acid gas (H_2S, CO_2) is removed by absorption in diethanolamine (DEA) or other similar solvents in the amine wash tower followed by a caustic wash step. The amine stripper strips the acid gas (Stream 22) from the saturated DEA and the DEA (Stream 23) is recycled to the amine wash tower. Very little blowdown from the DEA cycle is required.

The waste caustic solution, blowdown from the DEA cycle, and wastewater from the caustic wash tower are neutralized, stripped of acid gas, and removed as liquid waste streams (Streams 24 and 25). The acid gas stripped from the DEA and caustic waste (Stream 22) passes to an emission control device (Vent D), primarily to control H_2S emissions.

Following acid gas removal, the remaining process gas stream (Stream 26) is further compressed and is then passed through drying traps containing a desiccant, where the water content is reduced to the low level necessary to prevent ice or hydrate formation in the low-temperature distillation operations. The drying traps are operated on a cyclic basis, with periodic regeneration necessary to remove accumulated water from the desiccant. The desiccant is regenerated with heated fuel gas and the effluent gas is routed to the fuel system. Fouling of the desiccant by polymer formation requires periodic replacement, which results in the generation of a solid waste (Stream 27). However, with a normal desiccant service life of possibly several years, this waste source is relatively minor.

The demethanizer separates a mixture of hydrogen and methane from the C_2 and heavier components of the process gas (Stream 28). The demethanizer overhead stream (hydrogen and methane) is further separated into hydrogen-rich and methane-rich streams (Streams 29 and 30) in the low-temperature chilling section. The methane-rich stream is used primarily for furnace fuel. Hydrogen is required in the catalytic hydrogenation operations.

The de-ethanizer separates the C_2 components (ethylene, ethane, and acetylene) (Stream 31) from the C_3 and heavier components (Stream 32). Following catalytic hydrogenation of acetylene to ethylene by the acetylene converter (Stream 33), the ethylene-ethane split is made by the ethylene fractionator. The overhead from the ethylene fractionator (Stream 34) is removed as the purified ethylene product, and the ethane fraction (Stream 35) is recycled to the ethane/propane cracking furnace.

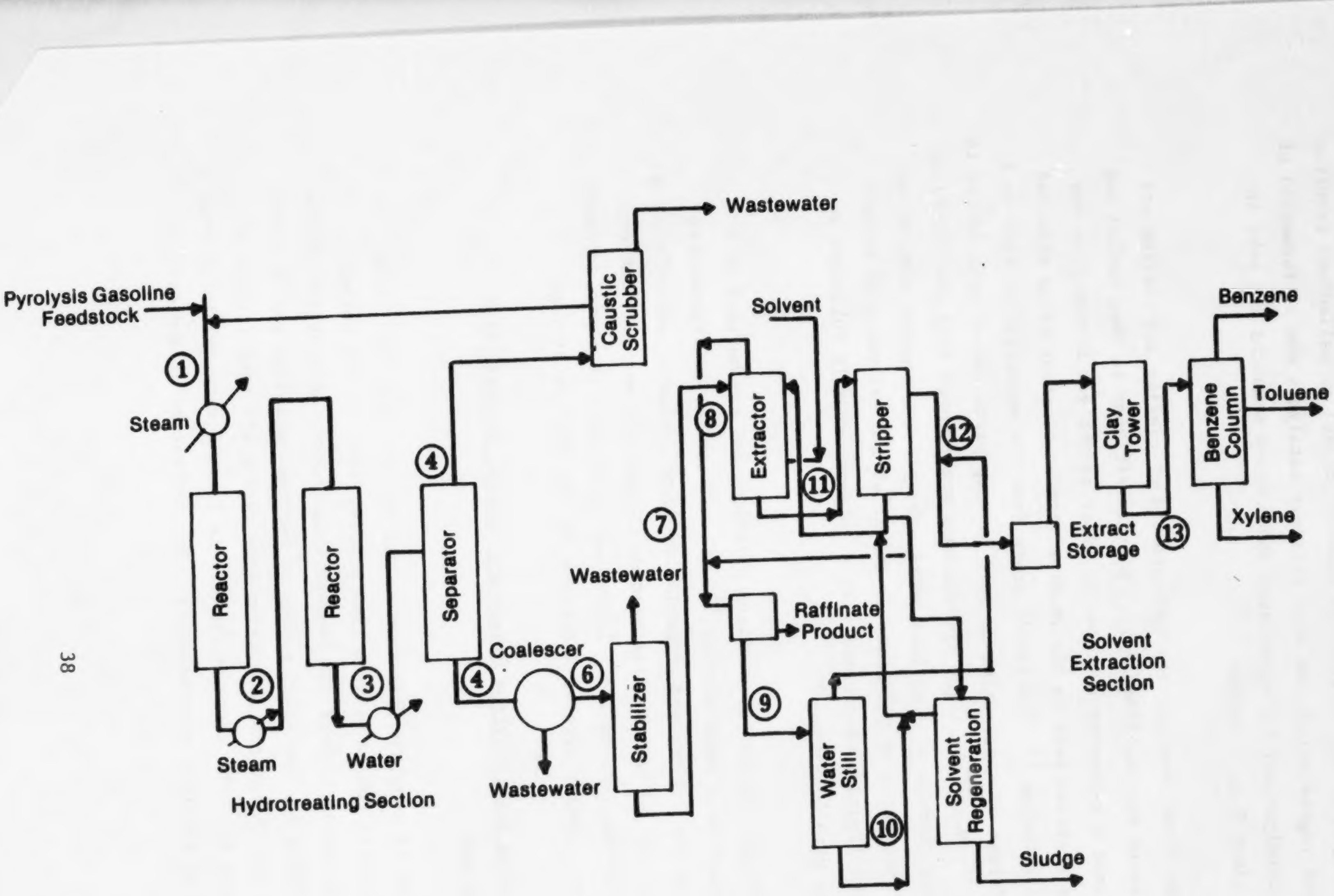
The de-ethanizer bottoms (C_3 and heavier compounds) (Stream 32) pass to the depropanizer, where a C_3-C_4 split is made. The depropanizer overhead stream (primarily propylene and propane) (Stream 36) passes to a catalytic hydrogenation reactor (C_3 converter), where traces of propadiene and methyl acetylene are hydrogenated. Following hydrogenation, the C_3 fraction passes to the propylene fractionator, where propylene is removed overhead as a purified product (Stream 37). The propane (Stream 38) is recycled to the ethane/propane pyrolysis furnace.

The C_4 and heavier components (Stream 39) from the depropanizer pass to the debutanizer, where a C_4-C_5 split is made. The overhead C_4 stream (Stream 40) is removed as feed to a separate butadiene process.

The stream containing C_5 and heavier compounds from the debutanizer (Stream 41) is combined with the bottoms fraction from the gasoline stripper as raw pyrolysis gasoline. The combined stream (Stream 42) is hydrogenated in the gasoline treatment section. Following the stripping of lights (Stream 43), which are recycled to the cracked-gas compressor, the C_5 and heavier compounds (Stream 44) are transferred to storage as treated pyrolysis gasoline. This stream contains benzene and other aromatics formed by pyrolysis.

The three catalytic hydrogenation reactors for acetylene, C_3 compounds, and pyrolysis gasoline all require periodic regeneration of the catalyst to remove contaminants. The catalyst is generally regenerated every four to six months. At the start of regeneration, as superheated steam (Stream 45) is passed through a reactor, a mixture of steam and hydrocarbons leaving the reactor (Stream 46) is passed to the quench tower. After sufficient time has elapsed for stripping of organics (approximately 48 hours), the exhaust is directed to an atmospheric vent (Vent F) and a steam-air mixture is passed through the catalyst to remove residual carbon. This operation continues for an additional 24 to 48 hours. The presence of air during this phase of the regeneration prevents the vented vapor from being returned to the process.

Because the olefins and di-olefins present in pyrolysis gasoline are unstable in motor gasoline and interfere with extraction of aromatics, they are hydrogenated prior to extraction of aromatics.[3] The actual hydrogenation process routes used are determined by the final product that is desired.[10] For example, Figure 7 shows one method of producing benzene, toluene, and xylene. Pyrolysis gasoline is fed with make-up hydrogen into the first stage hydrogenation reactor (Stream 1) where olefins are hydrogenated. The reaction conditions are mild (40-95°C and 10-40 atmospheres pressure).[3]


Wastewater
Pyrolysis Gasoline Feedstock
Caustic Scrubber
Solvent
Benzene
1
Steam
Extractor
Stripper
Clay Tower
Benzene Column
Toluene
8
11
12
4
Reactor
Reactor
Separator
7
Extract Storage
13
Xylene
Wastewater
Raffinate Product
Coalescer
Solvent Extraction Section
2
3
4
6
Stabilizer
9
Water Still
Solvent Regeneration
Steam
Water
Wastewater
Hydrotreating Section
10
Sludge

Note : Stream numbers on the figure correspond to the discussion in the text for this process.

Figure 7. Production of BTX by Hydrogenating Pyrolysis Gasoline[11]

The catalyst in the first stage reactor (nickel or palladium) requires more frequent regeneration than most refinery catalysts due to formation of gums.[3,11] Catalyst may be regenerated about every 4 months and coke is burned off every 9 to 12 months.[3,11]

From the first reactor, the hydrogenated di-olefins and olefins are sent to a second reactor (Stream 2). Reactor effluent is then cooled and discharged into a separator (Stream 3). Part of the gas stream from the separator is recycled back to the reactor (Stream 4) after being scrubbed with caustic solution.[11] The liquid phase from the separator is sent to a coalescer (Stream 5) where water is used to trap particles of coke formed in the reactor.[11] Next, the light hydrocarbons are removed from the liquid in the stabilizer (Stream 6). At this point, the process becomes similar to the solvent extraction of reformate in the catalytic reforming of naphtha. The stabilized liquid is extracted with a solvent, usually Sulfolane or tetraethylene glycol (Stream 7).

The raffinate (Stream 8) contains paraffins and may be sent to a cracking furnace to produce olefins.[11] The solvent may be regenerated (Streams 9 and 10). Dissolved aromatics (benzene, toluene, and xylene) are separated from the solvent by distillation (Stream 11) and are then sent through clay towers (Stream 12). Individual components (benzene, toluene, and xylene) are finally separated (Stream 13) and sent to storage.

Benzene Emissions from Ethylene Plants and Benzene Recovery from Pyrolysis Gasoline

Production of ethylene from naphtha/gas oil does not emit large quantities of total VOC or benzene from process vents during normal operation.[9] Emission factors for benzene from sources at ethylene plants are shown in Table 5. The chief source of benzene emissions during normal operations is the charge gas compressor lubricating oil vent (Stream 47, Vent G in Figure 6). The emission factors in Table 5 were developed from data supplied by ethylene manufacturers. The derivation of the emission

TABLE 5. UNCONTROLLED AND CONTROLLED BENZENE EMISSION FACTORS FOR A HYPOTHETICAL ETHYLENE PLANT[9,a]

Source	Source Designation[b]	Uncontrolled Emission Factor g/Mg[c]	Controlled Emission Factor g/Mg[c]	Control Option	Percent Efficiency
Compressor lube oil vents[d]	G				
Single compressor train		0.200	---	None	---
Dual compressor train		0.400	---	None	---
Other normal process emissions	A, B, D, F	No significant benzene emissions (see text)	---	---	---
Intermittent emissions	E		79.2 - 15.8	Flares	90 - 98
Single compressor train		791.9			
Dual compressor train		101.1	10.1 - 2.0		
Storage tanks	C	147	22.1	Floating roof tank	85
Salt dome	H	No benzene emissions (see text)			
Fugitives[d]		45.9	8.8	Detection/correction of leaks	80.9
Secondary[d]	K	21.7	---	None	---

[a] Data are for a hypothetical plant using 50 percent naphtha/50 percent gas oil as feed and having an ethylene capacity of 544.2 Gg/yr.

[b] Source locations correspond to vents/streams shown in Figure 6.

[c] Factors expressed as g of benzene emitted per Mg ethylene produced.

[d] Derivation of emission factors for fugitive emissions are shown in Appendix A. Secondary emissions include those from wastewater treatment.

factors is shown in Appendix A. Most benzene emissions from ethylene plants are intermittent emissions that occur during plant startup and shutdown, process upsets, and emergencies (Vent E).[9] For example, benzene may be emitted from pressure relief devices, intentional venting of off-specification materials or depressurizing and purging of equipment for maintenance.[9] Charge gas compressor and refrigeration compressor outages are also potential sources of benzene. Emissions from these compressors are generally short-term in duration, but the pollutants may be emitted at a high rate. In general, intermittent emissions, all pressure relief devices, and emergency vents are routed through the main process vent (Vent E in Figure 6). The vent usually is controlled. The relief valve from the demethanizer is usually not routed to the main vent. But the valve is operated infrequently and emits mainly hydrogen and methane.[9]

Potential sources of benzene such as flue gas from the cracking furnace (Vent A), pyrolysis furnace decoking (Vent B), acid gas removal (Vent D), and hydrogenation catalyst regeneration (Vent F) generally are not significant sources of benzene.[9] Flue gas normally contains hydrogen, products of methane combustion, and emissions from pyrolysis furnace decoking consist of air, steam, carbon dioxide, carbon monoxide, and particles of unburned carbon.[9] Emissions from acid gas removal are hydrogen sulfide, sulfur dioxide, and carbon dioxide; these emissions are generally controlled to recover hydrogen sulfide as sulfur or convert hydrogen sulfide to sulfur dioxide. As discussed earlier, catalyst regeneration is infrequent and no significant concentrations of benzene have been reported as present in the emissions.[9]

Fugitive benzene emissions at ethylene plants may originate from pumps, valves, process sampling, and continuous process analysis. The derivation of the emission factors is shown in Appendix A. Storage of ethylene in salt domes is not a potential source of benzene emissions because the ethylene generally does not contain benzene.

The emission factor for benzene from storage tanks shown in Table 5 was derived from AP-42 equations.[9] No supporting data showing how the equations were applied were provided by the emission factor reference.

Secondary emissions include those associated with handling and disposal of process wastewater. The emission factor in Table 5 was derived from estimates of wastewater produced and the estimated percent of the total VOC emitted from the wastewater that is benzene (see Appendix A).

No data were available concerning benzene emissions from recovering benzene from pyrolysis gasoline. Likely sources include reactor vents, compressors, and any vents on the benzene column (Figure 7).

The primary control technique available for intermittent emissions of benzene (pressure relief valves, emergency vents) is flaring. Other control methods are not as attractive as flaring because the emissions are infrequent and of short duration. The estimated efficiency of flares is 90-98 percent.[9] Flares can be operated to achieve efficiencies of 98 percent, if not greater, by controlling operating conditions.[13] EPA research efforts have documented the efficiencies of flares. The reader may wish to consult Reference 13 for more details on flares.

Fugitive emissions may be controlled by inspection/maintenance plans or use of types of equipment such as tandem seal pumps.[9] Emissions from sampling lines can be controlled by piping sample line purge gas to the charge gas compressor or to a combustion chamber.[9] Streams from process analyzers may be controlled in the same manner.[9]

The primary means of controlling emissions from pyrolysis gasoline or naphtha feedstock storage is the use of floating roof tanks. Emissions can be reduced by 85 percent when internal floating roof devices are used.[9]

Process Description: Coke Oven Light Oil Distillation

Although most benzene is obtained from petroleum, some is recovered through distillation of coke oven light oil at coke by-product plants. Table 2 lists facilities which produce benzene from light oil. Light oil is a clear yellow-brown oil which contains coal gas components with boiling points between 0 and 200°C.[8] Most by-product plants recover light oil, but not all plants refine it. About 13-18 L of light oil can be produced from coke ovens producing 1 Mg of furnace coke (3-4 gal/ton). Light oil itself contains from 60 to 85 percent benzene.[16]

The coke by-product industry recovers various components of coke oven gas including coal tar, pitch, ammonium sulfate, naphthalene, and light oil. Because benzene is contained in the coke oven gas, benzene may be emitted from coke by-product plants which do not specifically recover or refine benzene. Table 6 lists coke by-product plants in the United States.[14] Figure 8 shows a process flow diagram for a representative by-product recovery plant. The figure does not necessarily reflect any given plant, nor does the figure include all possible operations that could be found at a given coke by-product facility. The number of units and the types of processes used at specific plants are available. For example, naphthalene recovery is not practiced at all plants and some plants do not separate benzene from the light oil. Therefore, it is advisable to contact a specific facility to determine which processes are used before estimating emissions based on data in this report.

Coke by-product plants convert coal to coke in coke ovens. About 99 percent of the United States production of coke uses the slot oven process; the remainder is produced with beehive ovens. The coking time affects the type of coke produced. Blast furnace coke results when coal is coked for about 18 hours. Foundry coke, which is less common and is of higher quality, results when coal is coked for about 30 hours.[16]

TABLE 6. COKE OVEN BATTERIES CURRENTLY OPERATING IN THE UNITED STATES[14]

Plant, Location	Battery Identification Number	Status[a]
Dramon Company, Tarrant, AL	A	0
	5	0
	6	0
Empire Coke, Holt, AL	1	0
	2	0
Koppers, Woodward, AL	1	0
	2A	0
	2B	0
	4	0
	5	0
Gulf States, Gadsden, AL	2	0
	3	0
Jim Walters, Birmingham, AL	3	0
	4	0
	5	0
U. S. Steel, Fairfield, AL	2	2
	5	2
	6	2
	9	2
National Steel, Granite City, IL	A	0
	B	0
Interlake, Chicago, IL	1	0
	2	0
LTV Steel, South Chicago, IL	2	0
Bethlehem Steel, Burns Harbor, IN	1	0
	2	0
Citizens Gas, Indianapolis, IN	E	0
	H	0
	1	0

TABLE 6. COKE OVEN BATTERIES CURRENTLY OPERATING IN THE UNITED STATES[14] (Continued)

Plant, Location	Battery Identification Number	Status[a]
IN Gas, Terre Haute, IN	1	0
	2	0
Inland Steel, East Chicago, IN	6	0
	7	0
	8	0
	9	0
	10	0
U. S. Steel, Gary, IN	1	0
	5	0
	7	1
	13	1
	15	1
	16	1
LTV Steel, East Chicago, IN	4	2
	9	2
	3	2
Armco, Inc., Ashland, KY	3	0
	4	0
Bethlehem Steel, Sparrows Point, MD	1	2
	2	2
	3	2
	4	2
	5	2
	6	2
	11	0
	12	0
	A	0
Rouge Steel, Dearborn, MI	A	1
	C	1
National Steel, Detroit, MI	4	0
	5	2

TABLE 6. COKE OVEN BATTERIES CURRENTLY OPERATING IN THE UNITED STATES[14] (Continued)

Plant, Location	Battery Identification Number	Status[a]
Carondolet, St. Louis, MO	1	0
	2	0
	3	0
Bethlehem Steel, Lackawanna, NY	7	0
	8	0
	9	0
LTV Steel, Warren, OH	4	0
Armco, Inc., Middletown, OH	1	0
	2	0
	4	0
New Boston, Portsmouth, OH	1	0
Koppers, Toledo, OH	C	0
LTV Steel, Cleveland, OH	1	0
	2	0
	3	0
	4	2
	6	0
	7	0
U. S. Steel, Lorain, OH	D	2
	G	2
	H	2
	I	2
	J	2
	K	2
	L	2
Dramon Company, Keystone, PA	3	2
	4	2
Bethlehem Steel, Bethlehem, PA	A	0
	2	0
	3	0
	5	2

TABLE 6. COKE OVEN BATTERIES CURRENTLY OPERATING IN THE UNITED STATES[14] (Continued)

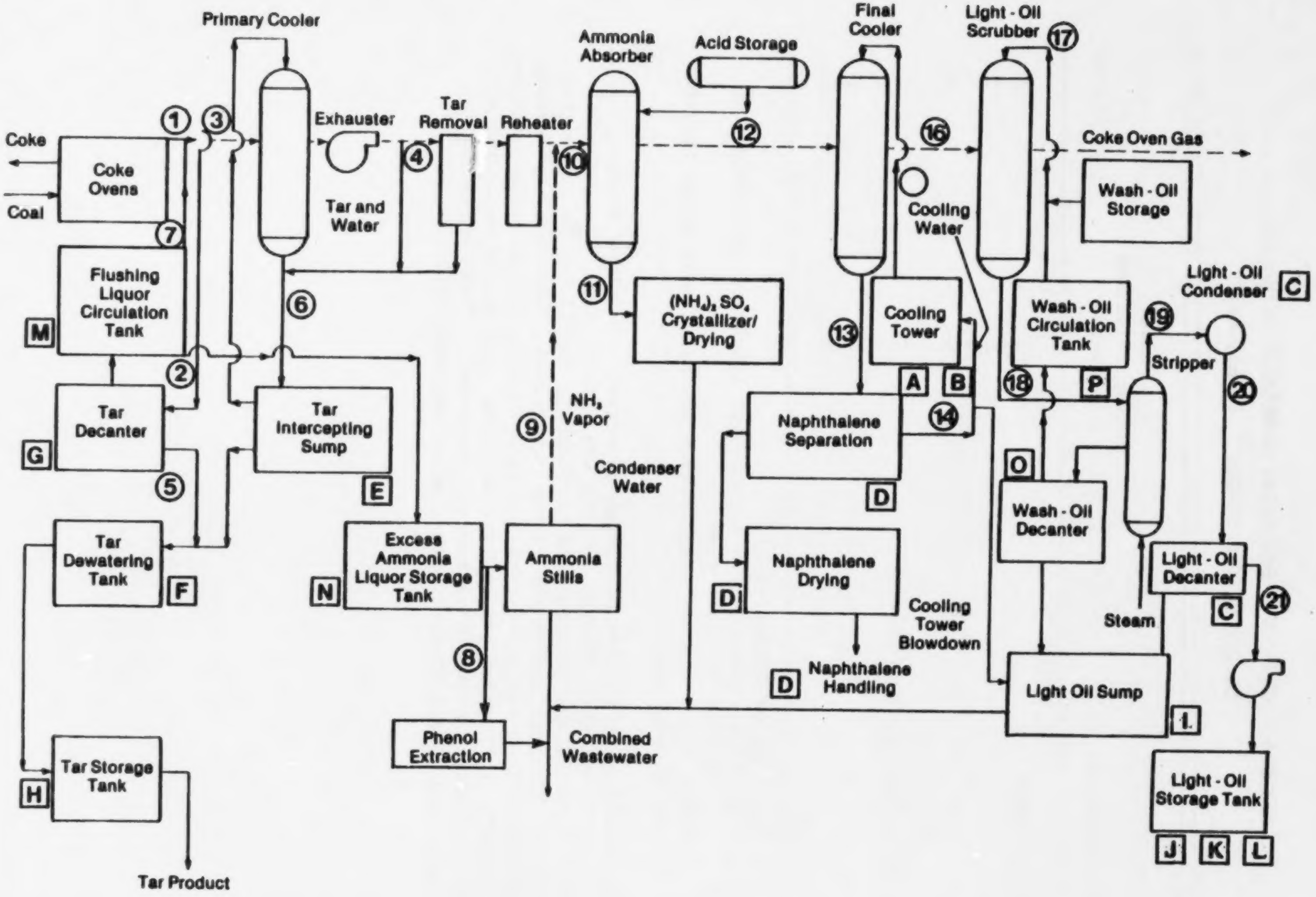
Plant, Location	Battery Identification Number	Status[a]
LTV Steel, Aliquippa, PA	A1	2
	A5	2
LTV Steel, Pittsburgh, PA	P1	0
	P2	0
	P3N	0
	P3S	0
	P4	0
Koppers, Erie, PA	A	0
	B	0
Shenango, Pittsburgh, PA	1	0
	4	0
U. S. Steel, Clairton, PA	1	0
	2	0
	3	0
	7	0
	8	0
	9	0
	15	1
	19	0
	20	0
	21	2
	22	2
	B	0
U. S. Steel, Fairless Hills, PA	1	2
	2	2
Wheeling-Pitt, Monessen, PA	1A	2
	1B	1
	2	1
Southern, Chattanooga, TN	1	0
	2	0
Lone Star Steel, Lone Star, TX	C	1

TABLE 6. COKE OVEN BATTERIES CURRENTLY OPERATING IN THE UNITED STATES[14] (Continued)

Plant, Location	Battery Identification Number	Status[a]
U. S. Steel, Provo, UT	1	1
	2	1
	3	1
	4	1
Wheeling-Pitt, East Steubenville, WV	1	0
	2	0
	3	0
	8	0

[a] Status: 0 - on-line or operating.
1 - hot idle, removed from service but likely to be returned to production in short time.
2 - cold idle, removed from service and not likely to be returned to production.

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particulate facilities by consulting current listings and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel. These operating plants and locations are current as of December 1987.


Primary Cooler
Ammonia Absorber
Acid Storage
Final Cooler
Light - Oil Scrubber
17
Coke
Coal
Coke Ovens
1
3
7
Exhauster
Tar Removal
Reheater
4
10
12
16
Coke Oven Gas
Tar and Water
Wash - Oil Storage
Cooling Water
Flushing Liquor Circulation Tank
M
6
11
(NH₄)₂SO₄ Crystallizer/ Drying
13
Cooling Tower
Wash - Oil Circulation Tank
Light - Oil Condenser
C
19
Stripper
2
A
B
18
P
20
Tar Decanter
G
Tar Intercepting Sump
E
NH₃ Vapor
9
Naphthalene Separation
14
D
O
5
Condenser Water
Wash - Oil Decanter
Tar Dewatering Tank
F
Excess Ammonia Liquor Storage Tank
N
Ammonia Stills
Naphthalene Drying
D
Light - Oil Decanter
C
21
Cooling Tower Blowdown
Steam
8
Naphthalene Handling
D
Light Oil Sump
I
Phenol Extraction
Combined Wastewater
Tar Storage Tank
H
Light - Oil Storage Tank
J
K
L
Tar Product

Note : The Stream numbers in circles on the figure correspond to the discussion of this process in the text. The emission sources are indicated with letters that correspond to Table 7.

Figure 8. Coke Oven By-Product Recovery, Representative Plant[16,17]

The coking process is actually thermal distillation of coal to separate volatile and nonvolatile components. Pulverized coal is charged into the top of an empty, but hot, coke oven. Peaks of coal form under the charging ports and a leveling bar smooths them out. After the leveling bar is withdrawn, the topside charging ports are closed and the coking process begins.

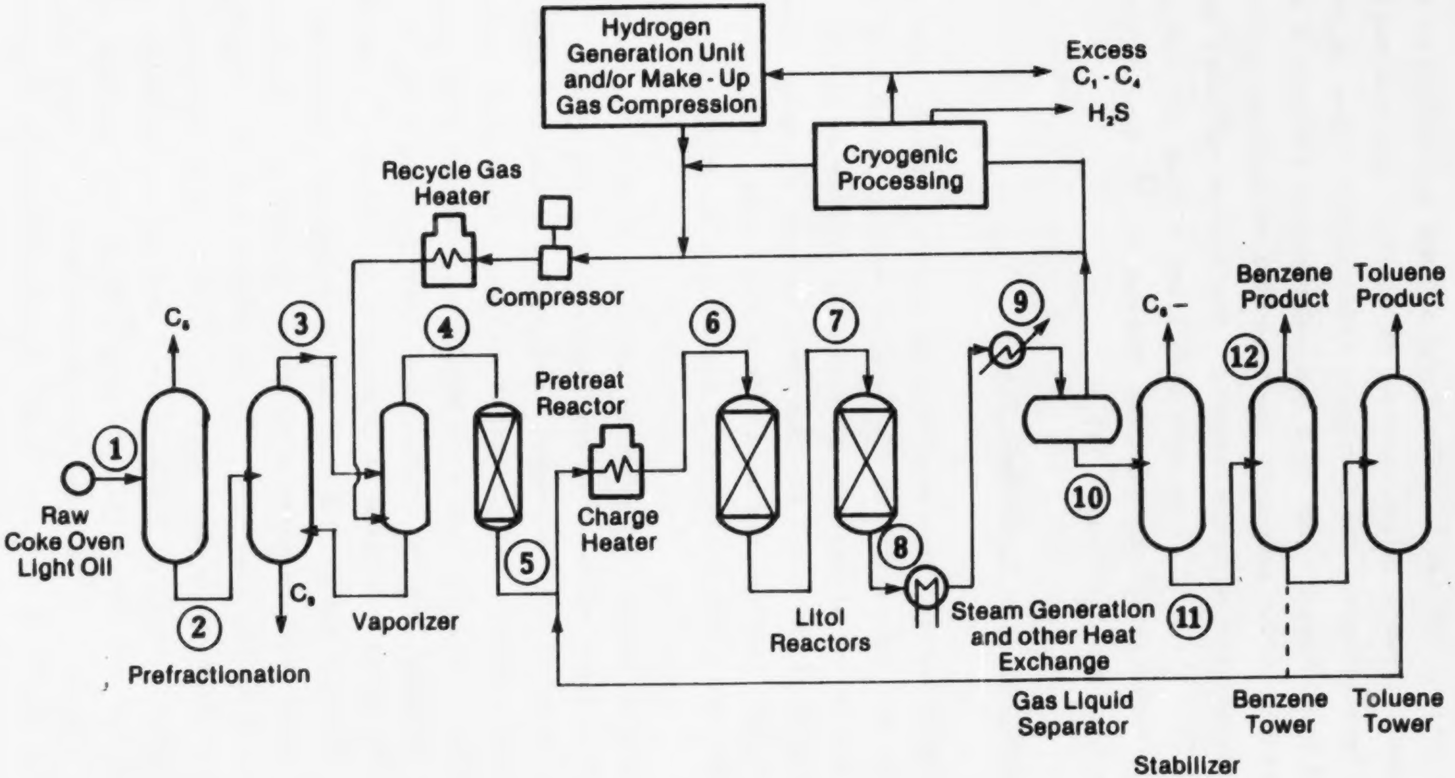
Heat for the coke ovens is supplied by a combustion system under the coke oven. The coking process requires about 15-18 hours to produce blast furnace coke and 25-30 hours for foundry coke.[15] The gases that are evolved during the thermal distillation are removed through the offtake main (Figure 8) and sent to the by-product plant for recovery.

As shown in Figure 8, coke oven gas leaves the oven at about 700°C and immediately is contacted with a cooling spray (Stream 1). The spray reduces the temperature of the gas and acts as a collecting medium for condensed tar. The gas then passes into the suction main. About 80 percent of the tar is separated from the gas in the mains and is flushed to the tar decanter (Stream 2).[16] Another 20 percent of the tar is condensed and collected in the primary cooler (Stream 3).[17] Smaller amounts of tar are removed from the gas by collectors (electrostatic precipitators or gas scrubbers) (Stream 4).[16] The tar is then separated from the flushing liquor by gravity and sent to the tar dewatering tank (Stream 5). The tar decanter generally separates "heavy" tar from flushing liquor and the primary cooler decanter (or primary cooler intercepting sump) accepts "light" tar which is cleaner and less viscous (Stream 6).[16] Depending on plant design, these two tar streams (Streams 5 and 6) may be merged or separated. Tar from the decanters is further dewatered in the tar dehydrator (Stream 5), and the separated water is recirculated (Stream 7). Tar may be sold to coal tar refiners or it may be refined on-site. Tar and tar products are stored on-site in tanks. Wastewater processing can recover phenol (Stream 8) and ammonia, with the ammonia routinely being reinjected into the gas stream (Stream 9). Ammonia salts or ammonia can be recovered by several processes. Traditionally, the ammonia-containing coke oven gas is contacted with sulfuric acid (Stream 10) and ammonium sulfate crystals are recovered

(Stream 11). The coke oven gas from which tar and ammonia have been recovered is sent to the final cooler (Stream 12). The final cooler is generally a spray tower, with water serving as the cooling medium.[16] Three types of final coolers and naphthalene recovery technologies are currently used: (1) direct cooling with water and naphthalene recovery by physical separation, (2) direct cooling with water and naphthalene recovery in the tar bottom of the final cooler, and (3) direct cooling with wash oil and naphthalene recovery in the wash oil.[16] Most plants use direct water final coolers and recover naphthalene by physical separation.[16] In this method, naphthalene in the coke oven gas is condensed in the cooling medium and is separated by gravity (Stream 13). After the naphthalene is separated, the water is sent to a cooling tower (Stream 14) and recirculated to the final cooler (Stream 15). The coke oven gas which leaves the final cooler is sent to the light oil processing segment of the plant (Stream 16).

As shown in Figure 8, light oil is primarily recovered from coke oven gas by continuous countercurrent absorption in a high boiling liquid from which it is stripped by steam distillation.[3] Coke oven gas is introduced into a light oil scrubber (Stream 16). Packed or tray towers have been used in this phase of the process, but spray towers are now commonly used.[3] Wash oil is introduced into the top of the tower (Stream 17) and is circulated through the contacting stages of the tower at around 1.5-2.5 L/m^3 of coke oven gas.[17] At a temperature of about 30°C, a light oil scrubber will remove 95 percent of the light oil from the coke oven gas. The benzene-containing wash oil is steam stripped (Stream 18) to recover the light oil.[17] Steam and stripped vapors are condensed and separated (Streams 19 and 20). The light oil is sent to storage (Stream 21).[16,17]

To recover the benzene present in the light oil, processes such as Litol (licensed by Houdry) or Hydeal (licensed by UOP) are used. Figure 9 shows a process diagram of the Litol process. The following discussion of the Litol process is drawn from a published description of the process.[18] The light oil is prefractionated (Stream 1) to remove the C_5 and lighter fractions, and the C_9 and heavier fractions (Stream 2). The remaining "heart cut" is sent to a vaporizer where it contacts gas with a


Hydrogen Generation Unit and/or Make - Up Gas Compression
Excess C_1 - C_4
H_2S
Cryogenic Processing
Recycle Gas Heater
Compressor
C_5
① ② ③ ④ ⑤ ⑥ ⑦ ⑧ ⑨ ⑩ ⑪ ⑫
Pretreat Reactor
Raw Coke Oven Light Oil
Charge Heater
C_9
Vaporizer
Prefractionation
Litol Reactors
Steam Generation and other Heat Exchange
C_5 –
Benzene Product
Toluene Product
Gas Liquid Separator
Benzene Tower
Toluene Tower
Stabilizer

Note : Stream numbers on the figure correspond to the discussion in the text for this process.

Figure 9. Litol Process Flow Diagram[18]

high-hydrogen content (Stream 3). The light oil and hydrogen then flow to a pretreat reactor (Stream 4) where styrene, di-olefins, and some sulfur compounds are hydrogenated. The partially hydrogenated stream is heated (Stream 5) and sent through a set of fixed bed reactors (Streams 6 and 7), where all remaining sulfur compounds are converted to hydrogen sulfide and organics are dehydrogenated or dealkylated. The reactor effluent is cooled (Streams 8 and 9). The product is then stabilized (Stream 10) and benzene is recovered by conventional distillation (Stream 11).[18] Benzene product may then be sent to storage (Stream 12).

Benzene Emissions from Coke By-product Plants

Benzene may be emitted from many sources within a coke by-product plant; emissions are not limited to the benzene recovery section of the process. The coke ovens themselves are potential sources of benzene emissions. Sources of emissions at coke ovens include charging, leaking coke oven doors, and leaking coke oven lids and offtakes. Emissions from lids and offtakes are often collectively called topside emissions.

During charging, moist coal contacts the hot oven floor and walls, and, as a result, the release of volatile components begins immediately. Control of charging emissions is more dependent on operating procedures than on equipment. Control options include staged charging, sequential charging and use of wet scrubbers on larry cars (the mobile hoppers that discharge the coal). Staged charging involves pouring coal into the coke ovens so that an exit space for the gases generated is constantly maintained.[15] The hoppers delivering the coal are discharged such that emissions are contained in the ovens and collecting mains by steam aspiration. Generally, a maximum of two hoppers discharging at the same time. In sequential charging, the first hoppers are still discharging when subsequent hoppers begin discharging coal. As with staged charging, the coke ovens are under aspiration in sequential charging. The sequential charging procedure is designed to shorten the charging time. The final control method for charging emissions is the use of wet scrubbers on larry cars. With this control technique, the scrubber emissions are contained by hoods or shrouds that are lowered over the charging ports.

Another potential source of benzene emissions at coke ovens is leaking doors. The doors are sealed before the coking process begins. Some doors have a flexible metal band or rigid knife edge as a seal. The seal is formed by condensation of escaping tars on the door's metal edge. Other doors are sealed by hand by troweling a mixture into the opening between the coke oven door and door frame. After the coking process is complete, the doors are opened to push the coked coal out into special railroad cars called quench cars for transport to the quench tower. Quenched coke is then discharged onto a "coke wharf" to allow quench water to drain and to let the coke cool. Emissions occur during the coking process from leaks in door seals. Control techniques for leaking doors include oven door seal technology, pressure differential devices, hoods/shrouds over the doors, and use of more efficient operating/maintenance procedures.[15]

Oven door seal technology relies on the principle of producing a resistance to the flow of gases out of the coke oven. This resistance may be produced by a metal-to-metal seal, a resilient soft seal, or a luted seal. Small cracks and defects in the seal permit pollutants to escape from the coke oven early in the cycle. The magnitude of the leak is determined by the size of the opening, the pressure drop between the oven and the atmosphere, and the composition of the emission.

The effectiveness of a pressure differential control device depends on the ability of the device to reduce or reverse the pressure differential across any defects in the door seal. These systems either provide a channel to permit gases that evolve at the bottom of the oven to escape to the collecting main or the systems provide external pressure on the seal through the use of steam or inert gases.

Oven door emissions also can be reduced by collection of the leaking gases and particulates and subsequent removal of these pollutants from the air stream. A suction hood above each door with a wet electrostatic precipitator for fume removal is an example of this type of system.

Other control techniques rely on operating and maintenance procedures rather than only hardware. Operating procedures for emission reduction could include changes in the oven cycle times and temperatures, the amount and placement of each charge, and any adjustments of the end-door while the oven is on-line. Maintenance procedures include routine inspection, replacement, and repair of control devices and doors.

Topside leaks are those occurring from rims of charging ports and standpipe leaks on the top of the coke oven. These leaks are primarily controlled by proper maintenance and operating procedures which include:[15]

- replacement of warped lids;
- cleaning carbon deposits or other obstructions from the mating surfaces of lids or their seats;
- patching or replacing cracked standpipes;
- sealing lids after a charge or whenever necessary with a slurry mixture of clay, coal, and other materials (commonly called lute); and
- sealing cracks at the base of a standpipe with the same slurry mixture.

Luting mixtures are generally prepared by plant personnel according to formulas developed by each plant. The consistency (thickness) of the mixture is adjusted to suit different applications.

Emission factors were often not available specifically for benzene emissions at coke ovens. One test, examining emissions of door leaks, detected benzene in the emissions. The coke oven doors being tested were controlled with a collecting device, which then fed the collected emissions to a wet electrostatic precipitator. Tests at both the precipitator inlet and outlet showed benzene concentrations of 1 to 3 ppm (or about 3-10 mg/m^3). These data translated into an estimated benzene emission factor of 0.6 to 2.4 kg benzene per hour of operation for coke oven doors.[15] No further emission factors for benzene and coke ovens were found in the literature. However, an analysis of coke oven gas indicated a benzene content of 21.4 to 35.8 g $benzene/m^3$.

Other potential sources of benzene emissions associated with the by-product plant are given in Table 7 along with emission factors. Equipment leaks may also contribute to benzene emissions. Emission factors for pumps, valves, etc., are shown in Table 8. This section of the report describes the potential sources of benzene emissions listed in Tables 7 and 8. Emission sources and control technologies are described in groups of related processes, beginning with the final cooling unit.

The final cooler unit itself is not a source of benzene because coolers are closed systems. However, the induced draft cooling towers used in conjunction with direct water and tar bottom final coolers are potential sources of benzene. Benzene can be condensed in the direct-contact cooling water, and, in the cooling tower lighter components (such as benzene) will be stripped from the recirculating cooling water. The emission factor of 270 g/Mg coke (0.54 lb/ton) shown in Table 7 was based on actual measurements of benzene concentrations and volumetric gas flowrates taken from source testing reports.[16] Control technologies available for cooling tower emissions are conversions to different types of cooling towers. For example, a facility with a direct water final cooler could insert a one-stage mixer-settler into the final cooling process and thus obtain the benefits of a tar bottom cooler. Although a tar bottom cooler does not eliminate benzene emissions from the cooling tower, it does eliminate benzene emissions associated with the physical separation of naphthalene and water.

Use of a wash oil final cooler effectively eliminates the benzene emissions associated with direct water or tar bottom coolers because the wash oil is cooled by an indirect heat exchanger thereby eliminating the need for a cooling tower.[16] Wash oil is separated after it leaves the heat exchanger and recirculates back through the circulation tank to the final cooler.

As discussed earlier in this section, coke by-product plants may recover naphthalene by condensing it from the coke oven gas and separating it from the cooling water by flotation. Benzene may be emitted from most

TABLE 7. BENZENE EMISSION FACTORS FOR FURNACE AND FOUNDRY COKE BY-PRODUCT PLANTS[16]

Source	Source Identification Number[a]	Uncontrolled Emission Factor g/Mg[b,c]		Controlled Emission Factor g/Mg[b,c]		Control Option	Control Efficiency (%)
		Furnace Coke	Foundry Coke	Furnace Coke	Foundry Coke		
Cooling Tower							
Direct-water	A[d]	270	197	51	37.4	Use tar-bottom final cooler	81[f]
				---	---	Use wash-oil final cooler	100
Tar Bottom	B[d]	70	51	---	---	Use wash-oil final cooler	100
Light-oil Condenser Vent	C	89	48	1.8	0.9	Gas blanketing	98
Naphthalene Separation and Processing	D	107	79	---	---	e	---
Tar-intercepting Sump	E	90	45	1.9	0.9	Gas blanketing	98
Tar Dewatering	F	21	9.9	0.42	0.2	Gas blanketing	98
				2.1	0.9	Wash-oil scrubber	90
Tar Decanter	G	77	36	3.9	1.8	Gas blanketing	95
Tar Storage	H	12	5.6	0.24	0.1	Gas blanketing	98
				1.2	0.5	Wash oil scrubber	90
Light-oil Sump	I	15	8.1	0.3	0.2	Source enclosure	98
Light-oil Storage	J	5.8	3.1	0.12	0.06	Gas blanketing	98
				0.58	0.3	Wash-oil scrubber	90
BTX Storage	K[e]	5.8	3.1	0.12	0.06	Gas blanketing	98
				0.58	0.3	Wash-oil scrubber	90
Benzene Storage	L[e]	5.8	3.1	0.12	0.06	Nitrogen or natural gas blanketing blanketing system	98
				0.58	0.3	Wash-oil scrubber	90

TABLE 7. BENZENE EMISSION FACTORS FOR FURNACE AND FOUNDRY COKE BY-PRODUCT PLANTS[16] (Continued)

Source	Source Identification Number[a]	Uncontrolled Emission Factor g/Mg[b,c]		Controlled Emission Factor g/Mg[b,c]		Control Option	Control Efficiency (%)
		Furnace Coke	Foundry Coke	Furnace Coke	Foundry Coke		
Flushing-liquor Circulation Tank	M	9	6.6	0.18	0.13	Gas blanketing	98
Excess-ammonia Liquor Tank	N	9	6.6	0.18	0.13	Gas blanketing	98
						Wash-oil scrubber	90
Wash-oil Decanter	O	3.8	2.1	0.076	0.04	Gas blanketing	98
Wash-oil Circulation Tank	P	3.8	2.1	0.076	0.04	Gas blanketing	98

[a] Source identification numbers refer to locations identified in Figure 8.

[b] All factors for furnace coke are from Reference 16 and are based on work further described in this reference. Factors for foundry coke are taken from Reference 27. Control efficiencies are the same for both types of coke.

[c] Emission factors are expressed in terms of grams of benzene emitted per megagram coke produced.

[d] Usually only smaller plants use direct-water final cooler; all final coolers are shown as one unit in Figure 8.

[e] Not all plants separate BTX or benzene. Therefore all product storage is indicated in one box on the diagram in Figure 8.

[f] Includes 100 percent emission reduction for naphthalene processing and a 74 percent emission reduction for the direct-water final cooler tower.

TABLE 8. BENZENE EMISSION FACTORS FOR EQUIPMENT LEAKS AT FURNACE AND FOUNDRY COKE BY-PRODUCT PLANTS[16]

	Percent of Sources Leaking Initially	VOC Emission Factor, kg/Source Day	Furnace Plant Uncontrolled kg/Source Day[a,b]		Foundry Plant Uncontrolled kg/Source Day[a,b]		Control Option	Control Efficiency (%)
			Light Oil BTX Recovery[c]	Light Oil Recovery, Benzene Refining[c]	Light Oil BTX Recovery[c]	Light Oil Recovery, Benzene Refining[c]		
Valves	11	0.26	0.18	0.22	0.16	0.20	Quarterly inspection	63
							Monthly inspection	72
							Use sealed bellows valves	100
Pumps	24	2.7	1.9	2.3	1.7	2.1	Quarterly inspection	71
							Monthly inspection	83
							Use dual mechanical seals	100
Exhausters	35	1.2	0.28[c]	0.28[c]	0.25	0.25	Quarterly inspection	55
							Monthly inspection	64
							Use degassing reservoir vents	100
Pressure Relief Devices	d	3.9	2.7	3.4	2.5	3.1	Quarterly inspection	44
							Monthly inspection	52
							Use rupture disk system	100
Sampling Connections	d	0.36	0.25	0.31	0.23	0.28	Closed-purge sampling	100
Open-ended Lines	d	0.055	0.038	0.047	0.035	0.043	Plug or cap	100

[a] Factors for furnace coke are from Reference 16. They are based on the total VOC emissions from petroleum refineries and the percent of benzene in light oil and refined benzene. Factors for foundry coke are drawn from Reference 27. Control efficiencies are the same for both types of coke.

[b] Factors are expressed in terms of kg of benzene emitted per source day.

[c] Emission factors are presented for two different types of coke by-product plants, but are not representative of any particular plant.

[d] Based on uncontrolled emission factors and the control efficiency (%) given in this table.

naphthalene separation and processing operations.[16] Vapors from naphthalene separation tanks have been reported to contain benzene, benzene homologs, and other aromatic hydrocarbons.[16] The emission factors for naphthalene separation and processing shown in Table 7 are based on source testing data from a flotation unit, drying tank, and melt pit at a coke by-product recovery plant.[16]

Benzene may also be emitted from the light oil plant which includes the light oil condenser vent, decanter, storage tank, intercepting sumps, the wash oil decanter, circulation tank, and BTX storage. An available control technique is the use of gas blanketing with clean coke oven gas from the gas holder (or battery underfire system). With this technology, a positive pressure blanket of clean coke oven gas is piped to the light oil plant and the enclosed sources are connected to the blanketing line. Vapor emissions from the sources flow back into the clean gas system. Ultimate control of the vapors is accomplished by the combustion of the coke oven gas.[16] Such systems are currently in use at some by-product recovery plants and reportedly have operated without difficulty. The control efficiency is estimated to be about 98 percent.[16] The emission factors for benzene sources in the light oil plant shown in Table 7 are based on source tests.[16]

Sources of benzene emissions from tar processing include the tar decanter, tar intercepting sump, tar dewatering and storage, and the flushing liquor circulation tank. Emission factors for these sources are shown in Table 7.

Benzene emissions from the tar decanter are sensitive to two operating practices: residence time in the separator and optimal heating of the decanter.[16] These two variables should be kept in mind when using the emission factors presented in Table 7. Benzene is emitted from tar decanters through vents. Coke oven gas can be mechanically entrained with the tar and liquor that are fed into the decanter. Because tar is fed into the decanter at a slightly higher pressure, the coke oven gas will build up in the decanter if it is not vented.[16] Emissions were measured at tar decanters at several locations in the United States and the emission factor shown in Table 7 is the average of the test values.[16]

The water that separates from the tar in the decanter is flushing liquor and it is used to cool the coke oven gas leaving the coke oven. Excess flushing liquor is stored in the excess ammonia liquor tank. Benzene may be emitted from the flushing liquor circulation tank and the excess ammonia liquor tank. The emission factor of 9 g benzene/Mg coke was derived from a source test of fugitive emissions from a primary cooler condensate tank. It was assumed that the condensate tank contained liquids similar to the two sources of concern and that the tank was of a similar design.[16] The actual benzene emission rate from the flushing liquor circulation tank and excess ammonia liquor depends on the number of tanks, the number of vents, and the geometry of the tanks.[16]

The tar intercepting sump is a type of decanter which accepts light tar and condensate from the primary cooler. Some of this condensate may be used to make up flushing liquor and some may be forwarded to ammonia recovery.[16] No significant benzene emissions have been identified from the recovery of ammonia, but benzene can be emitted from the intercepting sump. An emission factor of 95 g/Mg coke was reported in the literature.[16]

Tar dewatering may be accomplished by steam heating or centrifugal separation or a combination of the two methods. Use of centrifugal separation will probably not be a source of benzene emissions directly, but benzene may be emitted as a fugitive emission if storage vessels are used.[17] In steam heating, benzene could be driven off in the vapors. The emission factor for tar dewatering in Table 7 was derived by averaging three factors based on source tests at tar dewatering tanks. The emission factors were 41, 9.5, and 12.9 g/Mg coke.[16]

The control technology applicable to sources of benzene from tar processing is gas blanketing. As described earlier in this section, gas blanketing has a control efficiency of 95 to 98 percent.[16]

The final group of sources of benzene emissions at coke by-product plants includes emissions from equipment leaks, such as pumps, valves, exhausters, pressure relief devices, sampling connection systems, and open ended lines. Emission factors for these sources are shown in Table 8. The factors in Table 8 were based on emission factors from a comprehensive survey of petroleum refineries and the percent of benzene in the liquid associated with each type of equipment.[16] Two different sets of emission factors are presented, one set for a plant practicing light oil and BTX recovery and one set for a plant producing refined benzene in addition to light oil. Emission factors for exhausters were derived by multiplying the VOC emission factor for compressors in hydrogen service and refineries by 0.235, the measured ratio of benzene to nonmethane hydrocarbons present in the coke oven gas at the exhausters.[16]

The control options available for equipment leaks involve quarterly or monthly inspections and maintenance, replacing equipment, or enclosing or plugging the leaking sections. Inspection/maintenance includes tightening seals, etc., as they are found during the inspection. The control efficiency for quarterly inspection and maintenance ranges from 40-70 percent and 50-80 percent for monthly inspections and maintenance. Replacing equipment or enclosing/plugging the sources eliminates the emissions.

Process Description: Petroleum Refineries

Crude oil contains small amounts of naturally occurring benzene. One estimate indicates that crude oil consists of 0.15 percent benzene by volume.[19] Therefore, some of the operations at petroleum refineries may emit benzene independent of specific benzene recovery processes. Table 9 lists the locations and capacities of petroleum refineries in the U. S. Most refineries are located along the Texas-Louisiana coastline of the Gulf of Mexico. A flow diagram of processes likely to be found at a model refinery is shown in Figure 10. (Note: In Table 9, calendar day means the time period midnight to midnight. Stream day means any 24-hour actual operation of a processing unit, regardless of calendar day.)

TABLE 9. UNITED STATES REFINERIES: LOCATION BY STATE AND CAPACITIES[20]

Company and Location[a]	Crude Capacity		Production Capacity, b/sd			
	b/cd[b]	b/sd[c]	Alky. *Poly.	Aromatics-isomerization	Lubes	Asphalt
ALABAMA						
Hunt Refining Co.--Tuscaloosa	44,500	47,600	.....	1,000	.....	10,500
Louisiana Land & Exploration Co.--Saraland	80,000	81,300	.....	6,000	.....	.....
ALASKA						
Atlantic Richfield Co.--Kuparuk	12,000	12,000	.....	.....	.....	.....
Prudhoe Bay	22,000	22,000	.....	.....	.....	.....
Chevron U.S.A. Inc.--Kenai	22,000	NR	.....	.....	.....	6,000
Mapco Petroleum Inc.--North Pole	70,000	70,000	.....	1,800	.....	2,000
Petro Star Inc.--North Pole	NR	6,000	.....	.....	.....	.....
Tesoro Petroleum Corp.--Kenai	72,000	80,000	.....	.....	.....	.....
ARIZONA						
Intermountain Refining Cl--Fredonia	5,000	NR	.....	.....	.....	1,000
ARKANSAS						
Berry Petroleum Co.--Stevens	3,500	4,000	.....	.....	.....	1,000
Cross Oil & Refining Co. of Arkansas--Smackover	6,800	7,200	.....	.....	3,500	2,000
Lion Oil Co.--El Dorado[1]	48,000	50,000	4,400	.....	.....	6,500
Mcmillan Ring-Free Oil Cl--Norphlet	5,870	6,000	.....	.....	2,600	2,000
Solvent Extraction: [1]5,500 b/d.						
CALIFORNIA						
Anchor refining Cl--McKittrick	10,000	11,000	.....	.....	.....	.....
Atlantic Richfield Co.--Carson	211,000	220,000	7,200 2,400	.....	.....	.....
Beacon Oil Co.--Hanford	17,300	19,100	.....	.....	.....	.....
Champlin Petroleum CO.--Wilmington	60,000	62,500	10,000	7,500	.....	.....
Chevron U.S.A. Inc.--Bakersfield	26,000	NR	.....	.....	.....	.....
El Segundo	405,000	NR	8,000	1,500	.....	.....
Richmond[1]	365,000	NR	9,200	2,000	11,700	11,000
Conoco Inc.--Santa Maria	9,500	10,000	.....	.....	.....	6,800
Edington Oil Cl--Long Beach	41,600	44,730	.....	.....	.....	15,554
Exxon Co.--Benicia	109,000	114,000	11,500	.....	.....	.....
Fletcher Oil & Refining Co.--Carson	29,500	30,500	.....	.....	.....	.....

TABLE 9. UNITED STATES REFINERIES: LOCATION BY STATE AND CAPACITIES[20] (Continued)

Company and Location	Crude Capacity		Production Capacity, b/sd			
	b/cd	b/sd	Alky. *Poly.	Aromatics-isomerization	Lubes	Asphalt
Golden Bear Division, Witco Chemical Corp.--Oildale	10,818	11,500	.....	.....	4,800	3,300
Golden West Refining Co.--Santa Fe Springs	40,600	42,300	3,000	.....	.....	4,000
Huntway Refining Co.--Benicia	8,400	9,000	.....	.....	.....	4,500
Wilmington	5,500	6,000	.....	.....	.....	4,500
Kern County Refinery Inc.--Bakersfield	21,400	23,000	.....	.....	.....	.....
Mcmillan Ring-Free Oil Cl--Signal Hill	13,000	14,300	.....	.....	.....	.....
Mobil Oil Corp.--Torrance	123,500	130,000	12,300	.....	.....	.....
Newhall Refining Cl--Newhall	21,400	23,00	.....	.....	.....	4,500
Oxnard Refinery--Oxnard	NR	4,500	.....	.....	.....	3,000
Pacific Refining Co.--Hercules	55,000	NR	.....	.....	.....	.....
San Joaquin Refining Cl--Bakersfield	18,000	20,000	.....	.....	.....	5,000
Shell Oil Co.--Martinez	113,500	117,000	8,000	3,200	4,500	11,000
Wilmington	111,000	116,000	8,600	.....	.....	.....
Superior Processing Co.--Santa Fe Springs	NR	46,000	2,400	1,000	.....	1,000
Texaco Refining & Marketing Inc.--Bakersfield	38,000	42,000	.....	.....	.....	.....
Wilmington	75,000	78,400	4,400	.....	.....	.....
Toxco Corp.--Martinez	126,000	132,600	10,500	.....	.....	.....
Unocal Corp.--Los Angeles	108,000	111,000	10,000	.....	.....	.....
Rodeo	118,000	125,100	.....	.....	5,100	.....

Solvent extraction: [1]50,000 b/sd.

Company and Location	b/cd	b/sd	Alky. *Poly.	Aromatics-isomerization	Lubes	Asphalt
COLORADO						
Asamera Oil U.S. Inc.--Commerce City	NR	40,000	*1,600	.....	.....	.....
Conoco Inc.--Commerce City	41,500	42,500	*2,000	.....	.....	3,300
DELAWARE						
Texaco Refining and Marketing Inc.--Delaware City	140,000	150,000	8,000	2,900	.....	.....
FLORIDA						
Young Refining Co.--St. Marks	17,500	19,000	.....	.....	.....	.....
GEORGIA						
Amoco Oil Co.--Savannah	28,000	30,000	.....	.....	.....	22,500
Young Refining Co.--Douglasville	7,000	6,500	.....	.....	1,000	4,000

TABLE 9. UNITED STATES REFINERIES: LOCATION BY STATE AND CAPACITIES[20] (Continued)

Company and Location	Crude Capacity b/cd	Crude Capacity b/sd	Production Capacity, b/sd Alky. *Poly.	Production Capacity, b/sd Aromatics-isomerization	Production Capacity, b/sd Lubes	Production Capacity, b/sd Asphalt
HAWAII						
Chevron U.S.A. Inc.--Barber's Point	48,000	NR	4,500	1,500	.....	1,300
Hawaiian Independent Refinery Inc.--Ewa Beach	61,500	67,900	.....	.....	.....	.....
ILLINOIS						
Calumet Industries Inc.--Burnham	.....	.....	.....	.....	750	.....
Clark Oil & Refining Corp.--						
Blue Island	64,600	68,000	6,000	.....	.....	4,500
Hartford	60,000	65,000	8,000	.....	.....	.....
Marathon Petroleum Co.--Robinson	195,000	205,000	7,600	10,000	.....	.....
Mobil Oil Corp.--Joliet	180,000	200,000	25,000	.....	.....	.....
Shell Oil Col.--Wood River	264,000	276,000	22,000	3,800	4,600	28,500
Unocal Corp.--Lemont	151,000	157,000	16,000	3,500	.....	3,500
INDIANA						
Amoco Oil Co.--Whiting	350,000	360,000	23,000	13,000	6,400	40,000
Indiana Farm Bureau Cooperative Association Inc.--Mt. Vernon	20,600	21,500	1,700	.....	.....	.....
Rock Island Refining Corp.--Indianapolis[1]	32,100	33,000	4,500	.....	.....	.....
Young Refining Corp.--Laketon	9,500	10,000	.....	.....	.....	3,500
KANSAS						
Derby Refining CO.--Wichita	28,800	30,000	3,000 1,500	.....	.....	.....
Farmland Industries Inc.--Coffeyville	56,500	60,723	6,000	.....	2,500	.....
Phillipsburg	26,400	27,460	.....	.....	.....	2,000
National Cooperative Refinery Association--McPherson	70,000	73,000	6,000	2,000 9,000	.....	.....
Texaco Refining & Marketing Inc.--El Dorado	80,000	82,000	10,000	2,969	.....	.....
Total Petroleum Inc.--Arkansas City	50,000	52,200	5,500	.....	.....	2,000
KENTUCKY						
Ashland Petroleum Co.--Catlettsburg[1]	213,400	220,000	12,000 *1,000	5,400 12,000	8,600	30,000

Solvent extraction: [1] 4,500.

TABLE 9. UNITED STATES REFINERIES: LOCATION BY STATE AND CAPACITIES[20] (Continued)

Company and Location	Crude Capacity		Production Capacity, b/sd			
	b/cd	b/sd	Alky. *Poly.	Aromatics-isomerization	Lubes	Asphalt
Somerset Refinery Inc.--Somerset	5,500	6,300	.....	.....	.....	.....
Solvent extraction: [1]10,000 b/sd.						
LOUISIANA						
Atlas Processing Co., Division of Pennzoil--Shreveport[1]	46,200	50,000	.....	.....	8,500	600
BP Oil Inc.--Belle Chasse	199,100	205,000	28,400	24,000 6,300	.....	.....
Calcasieu Refining Co.--Lake Charles	12,150	13,500	.....	.....	.....	.....
Calumet Refining Co.--Princeton	4,100	4,400	.....	.....	3,000	1,000
Canal Refining Co.--Church Point	7,858	7,858	.....	.....	.....	.....
Citgo Petroleum Corp.--Lake Charles	320,000	330,000	23,000	2,300	7,000	.....
Clairborne Gasoline Co.--Lisbon	NR	7,500	.....	1,500	.....	.....
Conoco Inc.--Lake Charles	156,500	164,000	6,000 *2,100	.....	.....	.....
Cotton Valley Refinery (Kerr-McGee Refining Corp.)--Cotton Valley	7,800	8,500	.....	.....	.....	.....
Exxon Co.--Baton Rouge[2]	455,000	474,000	29,800 *8,000	.....	17,400	28,900
Hill Petroleum Co.--	55,300	57,500	.....	.....	.....	.....
Marathon Petroleum Co.--Garyville	255,000	263,000	20,000	15,100	.....	25,000
Murphy Oil USA Inc.--Meraux[3]	92,500	95,400	8,700	.....	.....	.....
Placid Refining Co.--Port Allen[4]	46,000	50,000	3,500	.....	.....	.....
Shell Oil Co.--Norco	218,000	225,000	13,500 *10,000	.....	.....	.....
Tenneco Oil Co.--Chalmette	137,000	144,000	19,000	7,000	.....	.....
Texaco Refining & Marketing Inc.--Convent	225,000	240,000	12,500	.....	.....	.....
Solvent extraction: [1]7,100 b/sd. [2]6,900 b/sd. [3]12,000 b/sd. [4]5,000 b/sd.						
MICHIGAN						
Crystal Refining Co.--Carson City	4,000	6,200	.....	.....	.....	.....
Lakeside Refining CO.--Kalamazoo	5,600	NR	.....	.....	.....	.....
Marathon Petroleum Co.--Detroit	68,500	71,000	4,000	.....	.....	8,650
Total Petroleum.--Alma	40,000	42,000	4,200 1,000	.....	.....	.....

Dimersol.

TABLE 9. UNITED STATES REFINERIES: LOCATION BY STATE AND CAPACITIES[20] (Continued)

Company and Location	Crude Capacity		Production Capacity, b/sd			
	b/cd	b/sd	Alky. *Poly.	Aromatics-isomerization	Lubes	Asphalt
MINNESOTA						
Ashland Petroleum Co.--St. Paul Park	67,143	69,220	5,900 *350	8,000	.....	14,000
Koch Refining Co.--Rosemount	155,000	160,000	8,500 *1,100 3,700	.....	.....	35,000
Dimersol.						
MISSISSIPPI						
Amerada-Hess Corp.--Purvis	30,000	NR	3,500	.....	.....	.....
Chevron U.S.A. Inc.--Pascagoula	295,000	NR	16,200	5,500	.....	20,000
Ergon Refining Inc.--Vicksburg	20,500	22,000	.....	.....	2,000	12,000
Southland Oil Co.--Lumberton	5,800	6,500	.....	.....	.....	3,500
Sandersville	11,000	12,500	.....	.....	.....	5,100
MONTANA						
Cenex--Laurel[1]	40,400	42,500	3,000	2,000	.....	6,000
Conoco Inc.--Billings[2]	48,500	50,000	5,000	3,400	.....	6,500
Exxon Co.--Billings	42,000	44,000	2,700	.....	.....	3,000
Flying J. Inc.--Cut Bank	5,600	6,200	*500	.....	.....	.....
Montana Refining Co.--Great Fall	6,300	6,500	*350	.....	.....	.....
Solvent extraction: [1] 4,000 b/sd. [2] 8,500 b/sd (PDA).						
NEVADA						
Nevada Refining Co.--Tonopah	4,500	4,700	2,500	.....	.....	.....
NEW JERSEY						
Amerada-Hess Corp.--Port Reading	.....	.....	4,500 *5,000	.....	.....	.....
Chevron U.S.A. Inc.--Perth Amboy	80,000	85,000	.....	.....	.....	35,000
Coastal Eagle Point Oil Co.--Westville	90,000	95,000	3,000 *2,500	10,000 6,000	.....	.....
Exxon Co.--Linden	100,000	110,000	8,500	25,000	.....	38,000
Mobil Oil Corp.--Paulsboro	100,000	104,000	5,000	.....	8,500	.....
Seaview Petroleum Inc.--Thorofare	45,000	NR	.....	.....	.....	.....

TABLE 9. UNITED STATES REFINERIES: LOCATION BY STATE AND CAPACITIES[20] (Continued)

Company and Location	Crude Capacity		Production Capacity, b/sd			
	b/cd	b/sd	Alky. *Poly.	Aromatics-isomerization	Lubes	Asphalt
NEW MEXICO						
Bloomfield Refining Co.--Bloomfield	13,700	14,000	.....	.....	.....	.....
Giant Industries Inc.--Gallup	18,000	19,000	1,400	.....	.....	.....
Navajo Refining Co.--Artesia	NR	36,500	1,800	.....	.....	3,500
NORTH DAKOTA						
Amoco Oil Co.--Mandan	58,000	60,000	3,000 *1,700	4,000	.....	.....
Flying J Inc.--Williston	4,800	5,400	.....	.....	.....	.....
OHIO						
Ashland Petroleum Co.--Canton	66,000	68,000	7,000 *500	.....	.....	12,000
Chevron U.S.A. Inc.--Cincinnati	43,700	45,000	6,000	.....	.....	.....
Standard Oil Co. of Ohio--Lima	168,000	177,000	.....	24,400 6,500 16,600	2,100	.....
Toledo	120,000	126,000	11,300	.....	.....	7,000
Sun Cl--Toledo[1]	118,000	124,000	7,000	8,500 2,400	.....	.....
Solvent extraction: [1]11,000 b/sd.						
OKLAHOMA						
Conoco Inc.--Ponca City	134,000	138,000	12,000 *2,100	4,500	2,000	.....
Kerr-McGee Refining Corp.--Wynnewood[1]	43,000	45,000	5,000	.....	.....	5,000
Sinclair Oil Corp.--Tulsa	50,000		3,000	500	.....	2,500
Sun Cl--Tulsa	85,000	90,000	2,400	2,000 1,500 2,300	7,500	4,800
Total Petroleum Inc.--Ardmore	62,000	64,500	6,500	.....	.....	6,000
Solvent extraction: [1]5,000 b/sd.						
OREGON						
Chevron U.S.A. Inc.--Portland	15,000	15,789	.....	.....	.....	11,500

TABLE 9. UNITED STATES REFINERIES: LOCATION BY STATE AND CAPACITIES[20] (Continued)

Company and Location	Crude Capacity		Production Capacity, b/sd			
	b/cd	b/sd	Alky. *Poly.	Aromatics-isomerization	Lubes	Asphalt
PENNSYLVANIA						
Atlantic Refining & Marketing Corp.--Philadelphia	125,000	130,000	.....	.....	.....	25,000
BP Oil Inc.--Marcus Hook	168,000	177,000	8,200	.....	.....	.....
Chevron U.S.A. Inc.--Philadelphia	714,100	180,000	20,000	4,000 1,300	.....	.....
Kendall-Amalie Division, Witco Chemical Co.--Bradford	8,600	10,000	.....	.....	3,950	.....
Pennzoil Products Co.--Rouseville	15,700	16,500	.....	.....	4,750	.....
Quaker State Oil Refining Corp.--Farmers Valley	6,500	6,800	.....	.....	2,000	.....
Sun Cl--Marcus Hook	155,000	165,000	12,000	5,300	10,000	.....
United Refining Co.--Warren	60,000	62,000	3,000 *2,200	.....	.....	8,000
TENNESSEE						
Mapco Petroleum Inc.--Memphis	NR	60,000	3,000 *2,500	.....	.....	3,500
TEXAS						
Amber Refining CO.--Fort Worth	14,500	15,000	*600	.....	.....	.....
American Petrofina Inc.--Port Arthur	90,000	110,000	2,800	2,300 1,600	.....	.....
Amoco Oil CO.--Texas City	400,000	415,000	23,000	45,000 22,000	.....	.....
Atlantic Richfield Co.--Houston	278,000	290,000	9,000	11,000	6,400	.....
Champlin Petroleum Co.--Corpus Christi[1]	170,000	175,000	17,600 *1,600	2,500 1,500	.....	.....
Charter International Oil Co.--Houston[2]	NR	70,000	5,000	2,100	.....	5,500
Chevron U.S.A. Inc.--El Paso	76,000	NR	5,500	3,000	.....	5,500
Port Arthur	406,900	418,000	16,900	4,595 2,905 2,500 7,200	13,200	.....
Coastal States Petroleum Co.--Corpus Christi	95,000	NR	2,800	11,000 7,000	.....	10,000
Crown Central Petroleum Corp.--Houston	100,000	105,000	13,000	2,000 2,000	.....	.....
Diamond Shamrock Corp.--Sunray[3]	85,000	88,000	8,700 *4,600	1,400	.....	3,500
Three Rivers[4]	45,000	47,500	6,000	.....	1,000	.....

TABLE 9. UNITED STATES REFINERIES: LOCATION BY STATE AND CAPACITIES[20] (Continued)

Company and Location	Crude Capacity		Production Capacity, b/sd			
	b/cd	b/sd	Alky. *Poly.	Aromatics-isomerization	Lubes	Asphalt
Exxon Co. U.S.A.--Baytown[5]	494,000	525,000	29,000	.....	36,300	7,000
Fina Oil & Chemical Co. (subsidiary of American Petrofina)--Big Spring	NR	60,000	6,000	.....	.....	6,500
Howell Hydrocarbons Inc.--San Antonio	9,900	10,000	.....	.....	.....	.....
Koch Refining Co.--Corpus Christi	125,000	130,000	8,400	7,600 2,500	.....	.....
LaGloria Oil & Gas Co.--Tyler	65,000	70,000	4,800	.....	.....	.....
Liquid Energy Corp.--Bridgeport	10,000	10,800	.....	.....	.....	.....
Marathon Petroleum Co.--Texas City	69,500	72,000	11,000	2,500	.....	.....
Mobil Oil Corp.--Beaumont	270,000	285,000	13,000	20,000	8,300	.....
Phillips 66 Co.--Borger	100,000	105,000	14,000	3,060 8,100 12,100 12,500	.....	.....
Sweeny	175,000	195,000	10,500	5,575 7,630 9,100 7,800	.....	.....
Pride Refining Inc.-Abilene	42,750	45,000	.....	.....	.....	.....
Shell Oil Co.--Deer Park	228,500	240,000	7,800	19,100	10,000	6,900
Odessa	28,600	29,500	3,000	350	.....	.....
Southwestern Refining Cl--Corpus Christi	104,000	108,000	4,000 *4,200	6,500	.....	.....
Texaco Refining & Marketing Inc.--El Paso	17,000	18,000	1,500 *500	500	.....	.....
Port Arthur[6] and Port Neches	250,000	278,000	9,000	.....	15,800	14,000
Texas City Refining Inc.--Texas City	119,600	130,000	6,200	.....	.....	.....
Unocal Corp.--(Beaumont), Nederland	120,00	126,300	4,200 *1,400	5,000 1,800	3,100	2,400
Valero Refining Co.-Corpus Christi	NR	21,000	8,300 2,500	.....	.....	10,000

Solvent extraction: [1] 12,000 b/sd. [2] 10,000b/sd. [3] 1,000 b/sd. [4] 7,000 b/sd. [5] 53,000 b/sd. [6] 12,000 b/sd. Heavy oil cracker. Dimersol.

UTAH

Company and Location	b/cd	b/sd	Alky. *Poly.	Aromatics-isomerization	Lubes	Asphalt
Amoco Oil Co.--Salt Lake City	40,000	41,500	4,000	3,000	.....	.....
Big West Oil Co.--Salt Lake City	24,000	24,000	1,300	.....	.....	.....
Chevron U.S.A.--Salt Lake City	45,000	NR	4,300	750	.....	.....
Crysen Refining Inc.--Woods Cross	NR	12,500	.....	.....	.....	.....
Phillips 66 Co.--Woods Cross[1]	25,000	26,000	2,100	.....	.....	1,700
Seagull Refining Co.--Roosevelt	8,000	9,000	*2,200	.....	.....	.....

Solvent extraction: [1] 5,000 b/sd.

TABLE 9. UNITED STATES REFINERIES: LOCATION BY STATE AND CAPACITIES[20] (Continued)

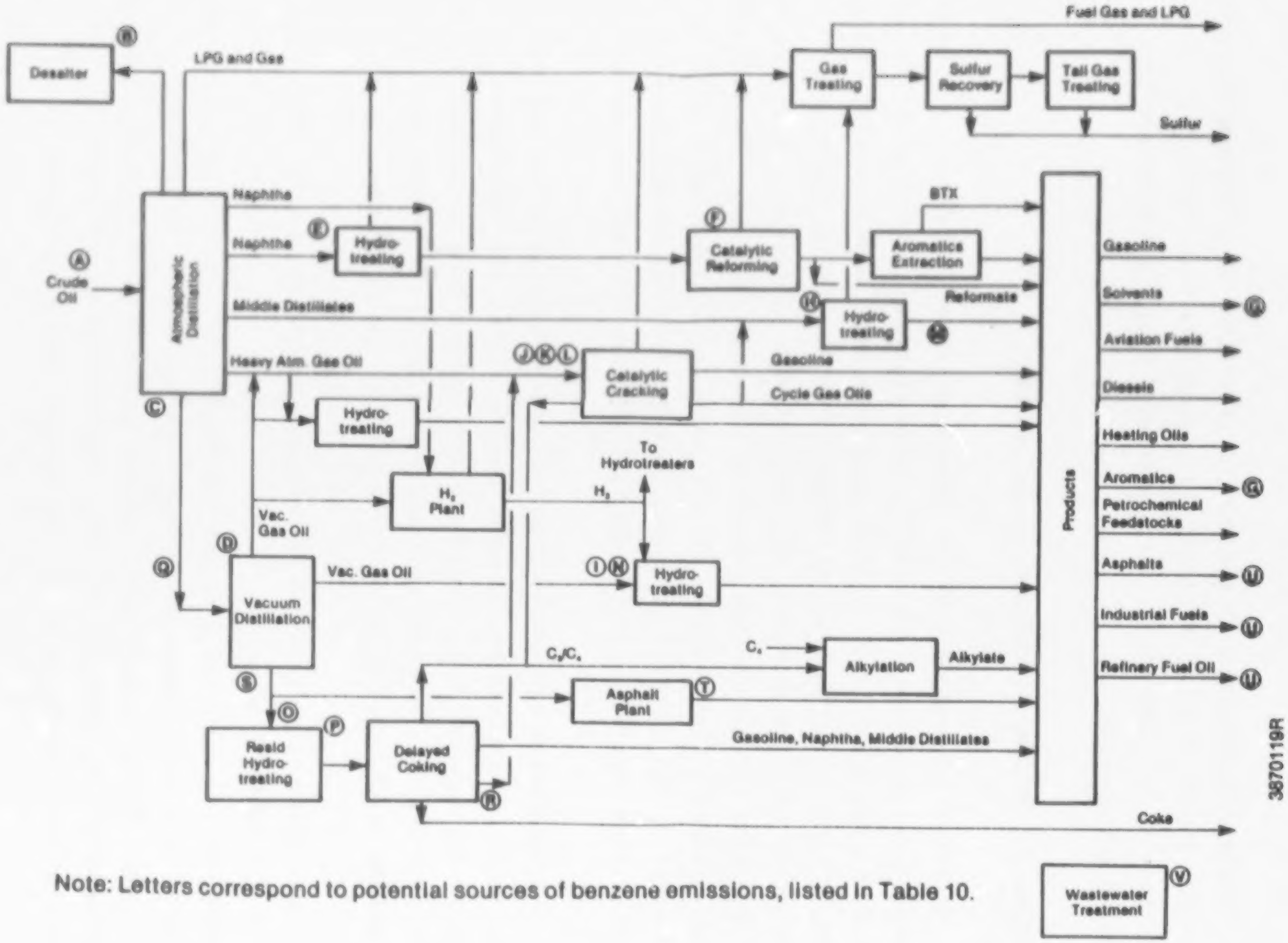
Company and Location[a]	Crude Capacity		Production Capacity, b/sd			
	b/cd[b]	b/sd[c]	Alky. *Poly.	Aromatics-Isomerization	Lubes	Asphalt
VIRGINIA						
Amoco Oil Co.--Yorktown	51,000	53,000	*2,400	.....	.....	.....
WASHINGTON						
Atlantic Richfield Co.--Ferndale	156,000	162,000	.....	.....	.....	.....
Chevron U.S.A. Inc.--Seattle	5,500	NR	.....	.....	.....	5,000
Mobil Oil Corp.--Ferndale	77,000	79,000	5,900	.....	.....	.....
Shell Oil Co.--Anacortes	72,000	75,000	12,100	2,900	.....	.....
Sound Refining Inc.--Tacoma	11,900	12,754	.....	.....	.....	6,000
Texaco Refining & Marketing Inc.--Anacortes[1]	78,000	82,000	6,600 *1,100	.....	.....	.....
U.S. Oil & Refining Co.--Tacoma	NR	31,000	.....	.....	.....	8,000

Solvent extraction: [1]7,400 b/sd.

Company and Location[a]	b/cd[b]	b/sd[c]	Alky. *Poly.	Aromatics-Isomerization	Lubes	Asphalt
WEST VIRGINIA						
Quaker State Oil Refining Corp.--						
Newell	11,700	12,000	.....	.....	3,600	.....
St. Mary's	4,800	5,000	.....	.....	1,400	.....
WISCONSIN						
Murphy Oil USA Inc.--Superior	32,000	34,000	1,700	.....	.....	13,500
WYOMING						
Amoco Oil Co.--Casper	40,000	41,000	1,700	.....	1,500	.....
Big West Oil Co.--Cheyenne	28,800	30,000	2,750	1,500	.....	3,700
Little America Refining Co.--Casper	NR	20,000	*400	.....	.....	.....
Mountaineer Refining Cl--LaBarge	NR	500	.....	.....	.....	.....
Sinclair Oil Corp.--Sinclair	53,000	54,000	4,000 *750	.....	.....	5,000
Wyoming Refining Co.--Newcastle	12,500	13,500	800	.....	.....	.....

a - As of January 1986. b - Barrels per calendar day. c - Barrels per stream day. *Polymerization. No asterisk means alkylation.

INACTIVE REFINERIES
1. Ashland Petroleum Co., Freedom, PA--6,800 bc/d.
2. Chevron U.S.A. Inc., Baltimore, MD--14,200 b/cd.
5. Gary Refining Co., Fruita, CO--15,200 b/cd.
6. Gladieux Refinery Inc., Ft. Wayne, IN--20,000 b/cd.
7. Kenco Refining Inc., Wolf Point, MT--4,700 b/cd.
8. Pester Refining Co., El Dorado, KS--31,000 b/cd.
9. Sabre Refining Inc., Bakersfield, CA--9,500 b/cd.
10. Texaco Inc., Amarillo, TX--20,000 b/cd.
11. Texaco Inc., Lawrenceville, IL--65,000 b/cd.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B
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Crude Oil
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Atmospheric Distillation
C
Naphtha
Naphtha
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Middle Distillates
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Tail Gas Treating
Fuel Gas and LPG
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C₃/C₄
C₄
Alkylation
Alkylate
Asphalt Plant
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Note: Letters correspond to potential sources of benzene emissions, listed in Table 10.

Figure 10. Process Flow Diagram for a Model Petroleum Refinery[21]

The specific processes which are potential sources of benzene emissions at petroleum refineries are listed in Table 10.

Complete description of the various operations at petroleum refineries is beyond the scope of this report. The reader is referred to References 21, 22, and 23 for descriptions of refining technology for detailed information.

Emissions of Benzene from Petroleum Refineries

Emissions of benzene from the processes listed in Table 10 are fugitive emissions, or emissions from catalyst regeneration.[21] No emission factors were found specifically for benzene emissions from these potential sources. Table 11 presents estimated concentrations of benzene in nonmethane hydrocarbon fugitive emissions for some refinery processes. Such data were not available for each of the processes listed in Table 10. The data in the table show that, for example, from the crude distillation unit, about 74 percent of the fugitive emissions from the unit may be attributed to the crude oil and that benzene constitutes 46 ppm (weight) of that stream.

The nonmethane hydrocarbon fugitive emissions from refineries occur from valves, pumps, drains, flanges, relief valves, and compressors. Emission factors for total nonmethane hydrocarbons from these sources are shown in Table 12. No emission factors were found for benzene or nonmethane hydrocarbon emissions from catalyst regeneration.

Some older literature has presented estimated benzene emission factors for entire refinery complexes.[26] These factors were based on an assumed benzene content of 0.1 to 1 percent in the various fugitive emissions and an assumed "very low" benzene content in catalytic cracker regenerator emissions. For an uncontrolled refinery, the estimated emission factor is 1 kg benzene/1000 barrel crude feed. For controlled refineries, the estimated emission factor is 0.19 kg benzene/1000 barrel crude feed.[26]

TABLE 10. POTENTIAL SOURCES OF BENZENE EMISSIONS AND PETROLEUM REFINERIES[21]

A	Crude storage
B	Desalting
C	Atmospheric distillation
D	Vacuum distillation
E	Naphtha hydrodesulfurization
F	Catalytic reforming
G	Light hydrocarbon storage and blending
H	Kerosene hydrodesulfurization
I	Gas oil hydrodesulfurization
J	Fluid bed catalytic cracking
K	Moving bed catalytic cracking
L	Catalytic hydrocracking
M	Middle distillate storage and blending
N	Lube oil hydrodesulfurization
O	Deasphalting
P	Residual oil hydrodesulfurization
Q	Visbreaking
R	Coking
S	Lube oil processing
T	Asphalt blowing
U	Heavy hydrocarbon storage and blending
V	Wastewater treating

TABLE 11. ESTIMATED CONCENTRATIONS OF BENZENE IN NONMETHANE HYDROCARBON FUGITIVE EMISSIONS FOR SELECTED REFINING PROCESSES[21]

Process/Unit	Process Streams (Percent of Total Fugitive Emissions Attributed to Stream)	Benzene Concentration of Stream (ppmw)[a]
Crude distillation	crude oil (74)	46
	straight run naphtha (24)	59
Aromatics extraction	reformate (12)	648
	aromatic extract (44)	7,850
	raffinate (44)	
Delayed coking	cracked naphtha (57)	1,642
Fluid catalytic cracking	cracked naphtha (45)	1,296
Hydrotreating	straight run naphtha (47)	119
	desulfurized naphtha (47)	119
Catalytic reforming	desulfurized naphtha (47)	119
	reformate (47)	2,538
Hydrogen production	straight run naphtha (19)	48

[a] Parts per million, by weight.

TABLE 12. EMISSION FACTORS FOR NONMETHANE HYDROCARBONS AND ESTIMATED BENZENE FRACTION AT PETROLEUM REFINERIES[21,24,25]

Emission Source	Process Stream Type	Uncontrolled Emission Factors (Kg/day-source)	Stream Composition (Weight Percent Benzene)[a]
Valves	gas/vapor	0.64	b
	light liquid	0.26	b
	heavy liquid	0.005	b
	hydrogen	0.20	b
Open end valves	all	0.05	b
Flanges	all	0.0061	0.10
Pump seals	light liquid	2.7	0.50
	heavy liquid	0.50	0.50
Compressor seals	gas/vapor	15	b
	hydrogen	1.2	b
Drains	all	0.76	2.4
Pressure relief valves	gas/vapor	3.9	b

[a] These data were not available for all streams. The data that were available were included in the interest of presenting as much data as possible.

[b] Species data for oil/gas production indicate possible benzene content of 0.10 weight percent in "unclassified fugitive emissions." These species data could be used to approximate benzene factor emissions.

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SECTION 5

EMISSIONS FROM INDUSTRIES USING BENZENE

Emission sources related to benzene's use as a feedstock and as a solvent are described in this section. Descriptions of benzene emissions from gasoline marketing operations and mobile sources are also included. Emission sources are identified and emission factors are presented as available. The reader is advised to contact the specific source in question to verify the nature of the process, production volume, and control techniques used before applying any of the emission factors presented in this report.

The largest portion of the total amount of benzene produced is used in production of ethylbenzene/styrene. Other major chemicals for which benzene is used as a feedstock include cyclohexane, cumene, phenol, nitrobenzene, and linear alkylbenzene.

Although benzene has been used in the production of maleic anhydride, the process is no longer used. All capacity for producing maleic anhydride in the United States is now n-butane based. The last facility using the benzene process has been placed on standby, with no stated intent of resuming operations. However, a brief description of the benzene process for maleic anhydride production is included in this section for reference.

ETHYLBENZENE PRODUCTION

Ethylbenzene is a liquid at standard conditions, having a boiling point of 136°C and a vapor pressure of 1284 Pa.[1] About 50 percent of the United States' production of benzene is used to produce ethylbenzene. The ethylbenzene industry is closely tied to the styrene industry since styrene is produced only from ethylbenzene. There can be approximately a 0.3 percent by weight carry-over of benzene into ethylbenzene and styrene.[2]

Additionally, some benzene is reformed in the production of styrene. Ethylbenzene production processes and uses thereby constitute a major potential source of benzene emissions, particularly since styrene is anticipated to show good growth through the 1980's. Due to increased process efficiency, ethylbenzene growth is anticipated to be slightly less (about 3 percent per year).[3]

Ethylbenzene is used almost exclusively to produce styrene. Some ethylbenzene is used as a solvent, often replacing xylene, and in the production of some dyes.[4] A total ethylbenzene production capacity of 4308 million kg/year currently exists.[3] Approximately 95 percent of this is based on benzene alkylation with the remainder based on extraction from mixed xylene streams. Most styrene is produced by two methods: hydrogenation of ethylbenzene (89 percent) and peroxidation of ethylbenzene with subsequent hydration (11 percent). The latter process can also co-produce propylene oxide. A third process, converting ethylbenzene isothermally to styrene, has been recently developed in Europe. To date, no United States facilities report using this method.

Another method which co-produces both ethylbenzene and styrene has been patented.[5] In this process, toluene and light alkanes other than ethane are reacted at 1000 to 1200°C and then gradually cooled to produce an 80 percent ethylbenzene/12 percent styrene product with a mass of about 25 percent by weight of the toluene reactant. These products can be separated by distillation and the ethylbenzene either recycled, sold, or converted to styrene by another process--dehydrogenation or peroxidation. This process is not reported to be in use at this time.

Table 13 lists United States producers of ethylbenzene and styrene. Most facilities produce both ethylbenzene and styrene on-site, thus reducing shipping and storage. Only two styrene production sites do not have an ethylbenzene production capacity. Ethylbenzene from mixed xylene separation is generally shipped or supplemented with another ethylbenzene source for styrene production. Only one site uses the peroxidation process to produce styrene. Table 13 also gives the latest facility capacity.

TABLE 13. UNITED STATES ETHYLBENZENE AND STYRENE PRODUCERS, LOCATION, AND CAPACITY[1,3,6]

Company	Location	Ethylbenzene		Styrene	
		Process	Capacity (Million lbs)	Process	(Million lbs) Capacity
American Hoechst	Bayport, TX	A	1035^a	---	---
	Baton Rouge, LA	---	---	C	900^a
ARCO	Houston, TX	B	110^b	---	---
	Port Arthur, TX	A	500^b	---	---
	Channelview, TX	A	1200^c	D	1200^c
	Beaver Valley, PA	---	---	C	220^a
Cosden	Big Spring, TX	B + purchased	103^b	C	110^b
Charter	Houston, TX	B	40^b	EB sold	---
Commonwealth	Panuelas, PR	B	161^b	EB sold	---
Cos-Mar	Carville, LA	A	1730^a	C	1500^a
Dow Chemical	Freeport, TX	A	1850^a	C	1301^a
	Midland, MI (idle)	---	---	C	324^a
El Paso	Odesa, TX	A	350^c	C	320^a
Chevron	St. James, LA	A	680^c	C	598^b
Monsanto	Alvin, TX	B	50^b	---	---
	Texas City, TX	A + B	1700^a	C	1500^a

TABLE 13. UNITED STATES ETHYLBENZENE AND STYRENE PRODUCERS, LOCATION, AND CAPACITY^{1,3,6} (Continued)

		Ethylbenzene		Styrene	
Company	Location	Process	Capacity (Million lbs)	Process	(Million lbs) Capacity
Standard Amoco Oil	Texas City, TX	A	985[b]	C	798[b]
Sun (Koch) Oil	Corpus Christi, TX	65% A 35% B	134[b]	C	80
Tenneco	Chalmette, LA	B	35[b]	EB sold	---
Union Carbide	Seadrift, TX	A	339[b]	C	299[b]
USX Corporation	Houston, TX	---	---	C	120

Key: Benzene Production	Styrene Production
A - Benzene Alkylation	C - EB Hydrogenation
B - Xylene Separation	D - EB Peroxidation and Dehydration

[a] Reference 6.

[b] 1977 production, from Reference 1.

[c] Reference 3.

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel. These data for producers and locations are current as of January 1986.

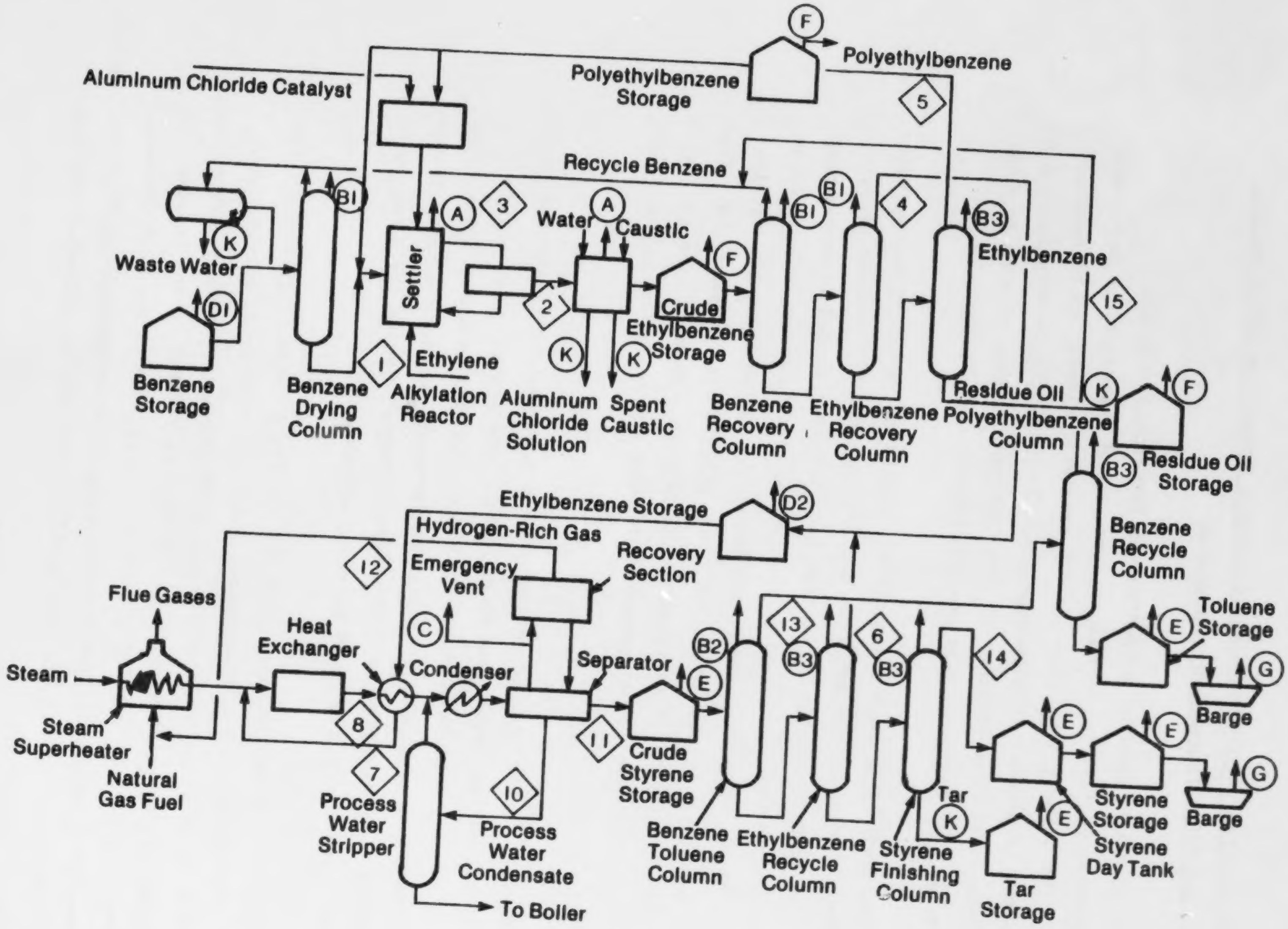
Process Description: Ethylbenzene and Styrene Production Using Benzene Alkylation and Ethylbenzene Dehydrogenation

Since most ethylbenzene production is integrated with the dehydrogenation process to produce styrene, these processes are described together. The primary reactions are (1) catalytic alkylation of benzene with ethylene to produce ethylbenzene, and (2) catalytic dehydrogenation of ethylbenzene to produce styrene. A detailed process flow diagram is shown in Figure 11. The process steps are described briefly as follows.

First, both fresh feed and recycled benzene are dried to remove water. Dry benzene (Stream 1) and ethylene are fed continuously into an alkylation reactor. A granular aluminum chloride catalyst is also fed at a constant rate. A temperature of 95°C is maintained by cooling water. The reactor effluent, which contains benzene, ethylbenzene, and an insoluble catalyst complex, goes to a settler where the crude ethylbenzene is decanted. The heavy catalyst complex is recycled to the reactor. Reactor vent gas (A) is routed to a condenser and scrubbers to recover any aromatics and to remove hydrogen chloride.

Pressure in the reactor can range from near ambient to about 2700 kPa and temperature may range from 80 to 400°C. One process uses a high pressure reactor with high-purity ethylene. In this process, inert gases are removed in a degassing step when the pressure on the alkylate effluent is removed. Another process (UOP or Mobil/Badger) uses a solid support catalyst with low-purity (5-10 percent) ethylene.

Next, crude ethylbenzene from the settler (Stream 2) is washed with water and neutralized with a caustic solution. The crude ethylbenzene contains 40 to 55 percent benzene, 10 to 20 percent polyethylbenzene (PEB), and high-boiling point materials. Benzene is removed in the benzene recovery column and recycled (Stream 3). Next, the product ethylbenzene (Stream 4) is separated from the remaining polyethylbenzene and high-boiling point materials. These are then distilled and the PEB recycled from the resultant residue oil.


Aluminum Chloride Catalyst
Polyethylbenzene Storage
F
Polyethylbenzene
5
Recycle Benzene
K
Waste Water
D1
Benzene Storage
B1
Benzene Drying Column
1
Settler
A
3
Ethylene
Alkylation Reactor
2
Water
A
Caustic
K
K
Aluminum Chloride Solution
Spent Caustic
F
Crude
Ethylbenzene Storage
B1
B1
4
B3
Ethylbenzene
15
Benzene Recovery Column
Ethylbenzene Recovery Column
Residue Oil
Polyethylbenzene Column
K
F
Residue Oil Storage
B3
Ethylbenzene Storage
D2
Hydrogen-Rich Gas
12
Emergency Vent
Recovery Section
C
Flue Gases
Steam
Steam Superheater
Natural Gas Fuel
Heat Exchanger
8
7
Condenser
Separator
Process Water Stripper
10
Process Water Condensate
To Boiler
11
E
Crude Styrene Storage
B2
13
B3
6
B3
14
Benzene Recycle Column
Toluene Storage
E
G
Barge
Benzene Toluene Column
Ethylbenzene Recycle Column
Styrene Finishing Column
Tar
K
E
E
E
G
Tar Storage
Styrene Storage
Styrene Day Tank
Barge

Note : Stream numbers refer to the discussion of this process in the text. Letters refer to potential sources of benzene emissions.

Figure 11. Process Flow Diagram for Production of Styrene From Benzene and Ethylene by Dehydration of Ethylbenzene[1,7]

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The purified ethylbenzene is preheated in a heat exchanger. The resultant vapor (Stream 7) is then mixed continuously with steam at 710°C in the dehydrogenation reactor which contains one of several catalysts. The reaction product (Stream 8) then exits through the heat exchanger. It is then further cooled in a condenser where water and crude styrene vapors are condensed. The hydrogen-rich process gas is recovered and used as a fuel (Stream 12) and the process water is purified in a stripper and recycled to the boiler. The remaining crude styrene liquid (Stream 11) goes to a storage tank. Benzene and toluene (Stream 13) are removed from the crude styrene in the benzene/toluene column. They are then typically separated by distillation. The toluene is sold and the benzene is returned to ethylbenzene production section (Stream 15), or it may also be sold. Next, the ethylbenzene column removes ethylbenzene which is directly recycled (Stream 6). Tars are removed and the product styrene emerges from the styrene finishing column. In some facilities, an ethylbenzene/benzene/toluene stream is separated from the crude styrene initially and then is processed separately.

Process Description: Ethylbenzene from Mixed Xylenes

Ethylbenzene can also be extracted from mixed xylene streams. Proportionately, however, very little ethylbenzene is produced in this fashion. The two major sources of ethylbenzene containing xylenes are (1) catalytic reformate from refineries, and (2) pyrolysis gasoline from ethylene production. The amount of ethylbenzene available is dependent on upstream production variables. The ethylene separation occurs downstream of the benzene production. For this reason, the ethylbenzene produced by this process is not considered a source of benzene emissions. Instead, benzene emissions from the entire process train are considered as emissions from benzene production and are included elsewhere in this report (Section 4).

When combined with the dehydrogenation process previously described to produce styrene (Figure 11), the process is similar except that the benzene recycling (Stream 15 in Figure 11) cannot be reused directly.

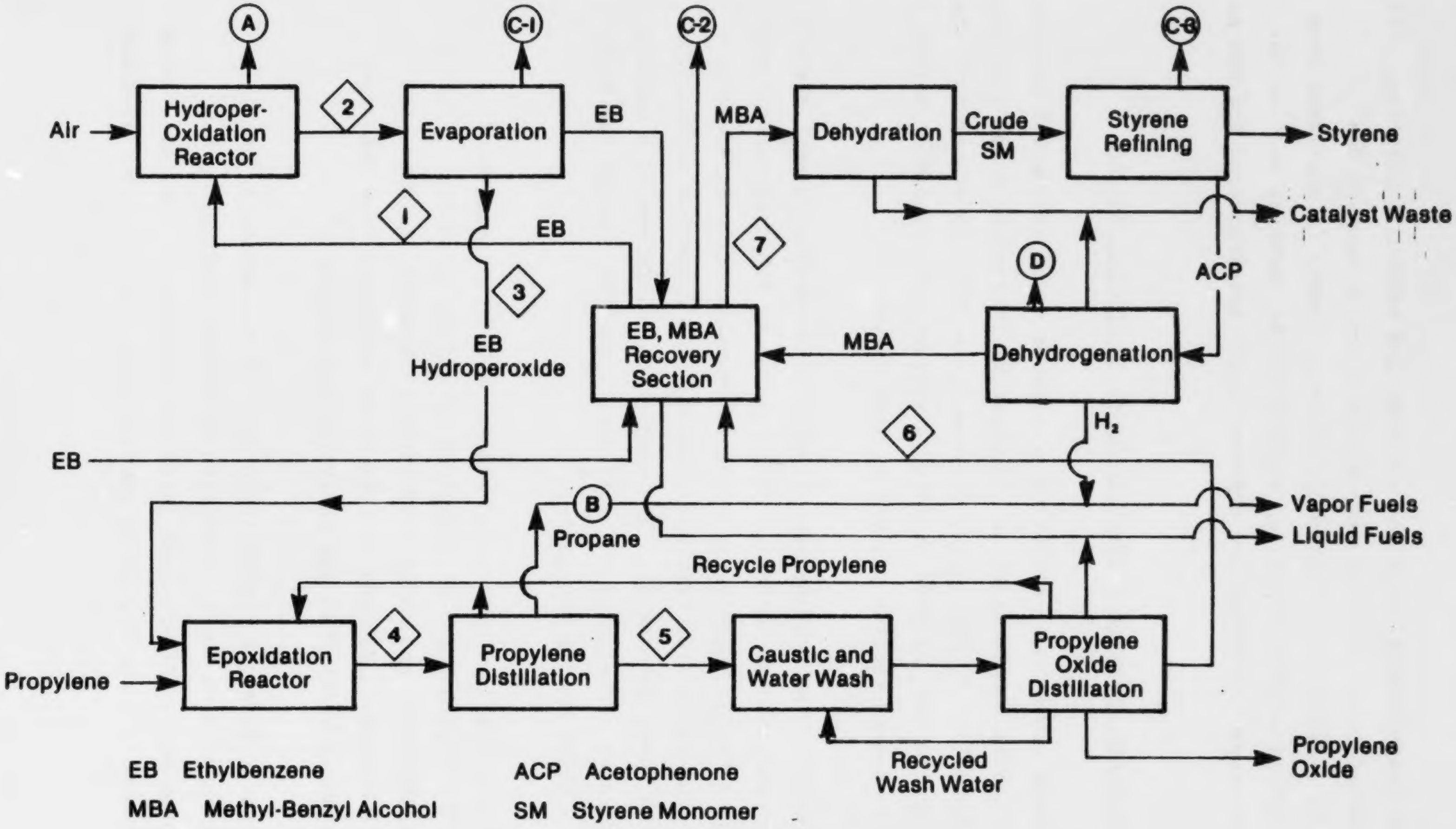
Process Description: Styrene from Ethylbenzene Hydroperoxidation

Presently, only one United States facility uses the hydroperoxidation process to produce styrene. Figure 12 gives a process flow diagram. The four major steps are described below.

Ethylbenzene (Stream 1) is oxidized with air to produce ethylene hydroperoxide (Stream 2) and small amounts of a-methyl-benzyl alcohol and acetophenone. The exit gas (principally nitrogen) is cooled and scrubbed to recover aromatics before venting. Unreacted ethylbenzene and low-boiling contaminants are removed in an evaporator. Ethylbenzene is then sent to the recovery section to be treated before reuse.

Ethylbenzene hydroperoxide (Stream 3) is combined with propylene over a catalyst mixture and high pressures to produce propylene oxide and acetophenone. Pressure is then reduced and residual propylene and other low-boiling compounds (Stream 4) are separated by distillation. The vent stream containing propane and some propylene can be used as a fuel. Propylene is recycled to the epoxidation reactor. The crude epoxidate (Stream 5) is treated to remove acidic impurities and residual catalyst material and the resultant epoxidate stream is distilled to separate the propylene oxide product for storage. Residual water and propylene are recycled to the process train and liquid distillate is recovered as a fuel. The organic layer is routed (Stream 6) to the ethylbenzene and a-methyl-benzyl alcohol recovery section. Distillation removes any remaining ethylbenzene and then separates organic waste streams from the a-methyl-benzyl alcohol and acetophenone organic waste liquids are used as fuel.

The mixed stream of a-methyl-benzyl alcohol and acetophenone (Stream 7) is then dehydrated over a solid catalyst to produce styrene. Residual catalyst solids and high-boiling impurities are separated and collected for disposal. The crude styrene goes to a series of distillation columns where the pure styrene monomer product is recovered. The residual organic stream


A
C-I
C-2
C-6
Air
Hydroper-Oxidation Reactor
2
Evaporation
EB
MBA
Dehydration
Crude SM
Styrene Refining
Styrene
Catalyst Waste
1
EB
7
D
ACP
3
EB Hydroperoxide
EB, MBA Recovery Section
MBA
Dehydrogenation
6
H_2
EB
B
Propane
Vapor Fuels
Liquid Fuels
Recycle Propylene
Propylene
Epoxidation Reactor
4
Propylene Distillation
5
Caustic and Water Wash
Propylene Oxide Distillation
Recycled Wash Water
Propylene Oxide
EB Ethylbenzene
MBA Methyl-Benzyl Alcohol
ACP Acetophenone
SM Styrene Monomer

Note : Stream numbers correspond to the discussion in the text for this process.
Letters represent potential sources of benzene emissions.

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Figure 12. Ethylbenzene Hydroperoxidation Process Block Diagram[7]

contains crude acetophenone, catalyst residue, and various impurities. This mixture is treated under pressure with hydrogen gas to convert the acetophenone to a-methyl-benzyl alcohol. Catalyst waste is separated from the a-methyl-benzyl alcohol which is returned to the recovery section for processing and reuse. Hydrogen and organic vapors are recovered for use as fuel.

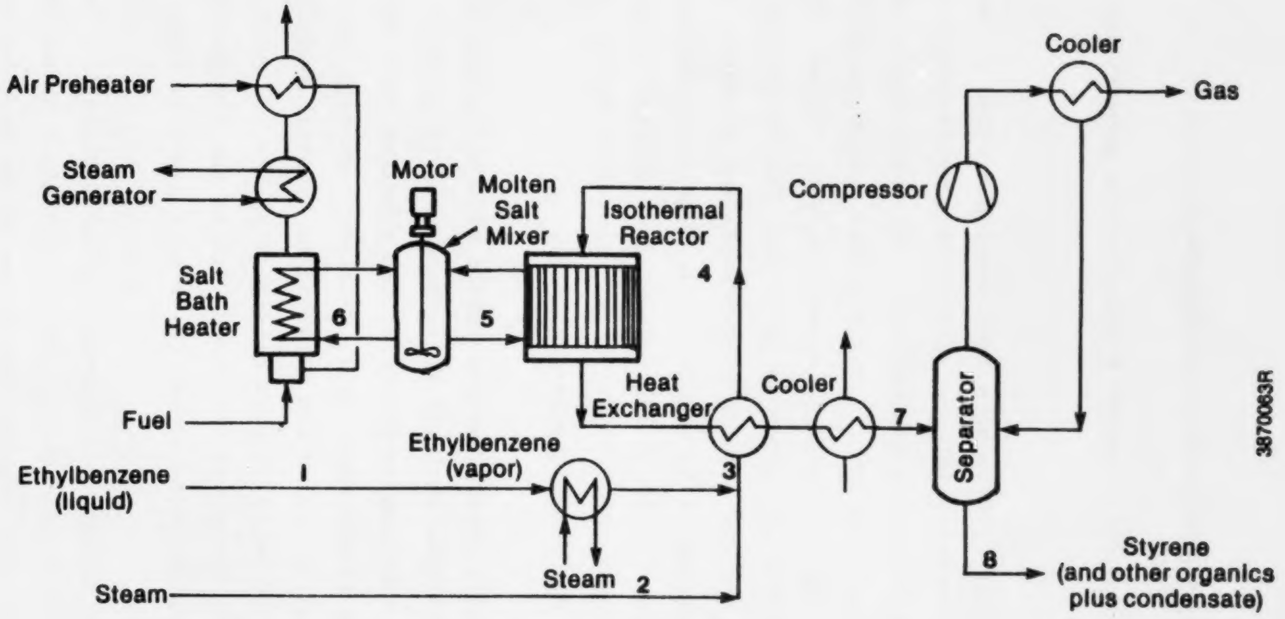
Process Description: Styrene Production by an Isothermal Method

Ethylbenzene may also be converted to styrene by an isothermal process (Figure 13). Liquid ethylbenzene is vaporized by condensing steam in a heat exchanger (Stream 1). Process steam (Stream 2) is then introduced into the ethylbenzene stream and the feed mixture is superheated (Stream 3) before it enters the molten-salt reactor (Stream 4) (see Figure 13).[8]

In the reactor, the ethylbenzene/steam mixture passes through the tubes where it comes into contact with the catalyst and is dehydrogenated. Heat for the dehydrogenation reaction is supplied by molten salt (preferably a mixture of sodium carbonate, lithium carbonate, and potassium carbonate) surrounding the tubes (Stream 5). The reactor is maintained at a uniform wall temperature by circulating the molten-salt mixture through the heat exchanger of a fired heater (Stream 6).[8]

The reaction products are cooled and condensed in a separator (Stream 7). The liquid phase is a mixture of organic products: styrene, unreacted ethylbenzene, and small quantities of benzene, toluene, and high-boiling compounds. Styrene (Stream 8) is separated from the other liquid constituents which then are recovered and recycled.[8]

The gas phase from the condensation step in the separator consists mainly of hydrogen, with small quantities of carbon dioxide, carbon monoxide, and methane. After these gases are compressed, they are cooled. Condensable products from this final cooling stage are then recovered and


Air Preheater
Steam Generator
Salt Bath Heater
Fuel
Ethylbenzene (liquid)
Steam
Motor
Molten Salt Mixer
Isothermal Reactor
Heat Exchanger
Ethylbenzene (vapor)
Steam
Cooler
Compressor
Cooler
Gas
Separator
Styrene (and other organics plus condensate)
1
2
3
4
5
6
7
8
3870063R

Note: Stream numbers correspond to the discussion in the text for this process.

Figure 13. Isothermal Processing of Styrene[8]

recycled to the separator. When hydrogen-rich offgas is used as fuel for the heater of the molten-salt reactor, the fuel requirement for this stage of the process is zero.[8]

Benzene Emissions from Ethylbenzene and Styrene Production

Emission Estimates from Ethylbenzene Production and Dehydrogenation to Styrene--

Estimated emission factors have been developed based on an uncontrolled 300 million kg/year capacity integrated ethylbenzene/styrene production plant. Major process emission sources are: the alkylation reactor area vents (A in Figure 11), atmospheric and pressure column vents (B-1), vacuum column vents (B-2), and the hydrogen separation vent (Stream 12). Emission rates from these sources are given in Table 14. The first four process vent streams in Table 14 are low-flow, high-concentration streams. The hydrogen separation stream (Stream 12 in Figure 11) is high-flow, low-concentration. Other emission sources listed in Table 14 include storage losses (D), (E), (F), and shipment losses (G). Fugitive emissions from valves and other equipment leaks are not indicated in Figure 11.

Reactor area vents remove various inerts plus entrained aromatics (benzene). Inerts include nitrogen or methane used in pressure control, unreacted ethylene, reaction by-products, and ethylene feed impurities. In typical plants using liquid phase $AlCl_3$ catalyst with high-purity ethylene, vent streams are usually cooled and scrubbed to recover aromatics. In plants using the newer solid support catalysts of the UOP or Mobil/Badger process, reactor vent flows are very large due to the low-purity ethylene feed. Process economics require that these vent gases be burned as fuel.

Atmospheric and column vents remove non-combustibles in the column feeds, light aliphatic hydrocarbons, and any entrained aromatics. The benzene drying column also removes impurities in the benzene feed. Most emissions occur in the first column of the distillation train (benzene recovery column in Figure 11).

TABLE 14. EMISSION FACTORS FOR ETHYLBENZENE/STYRENE PRODUCTION VIA ALKYLATION AND DEHYDROGENATION[a]

Emission Source	Source Location[b]	Uncontrolled g/kg	Control Device	% Efficiency	Controlled g/kg
Alkylation Reactor Area Vents	A	0.3^c	Process heater	99.9+	0.0003
Atmospheric/Pressure Column Vents	B-1	1.2^c	Flare	$60^c - 99^d$	0.012 - 0.48
Benzene-Toluene Vacuum Vent	B-2	3.0^c	Flare	$60^c - 99^d$	0.03 - 1.2
Other Vacuum Vents	B-3	0.05^c	Flare	$60^c - 99^d$	0.0005 - 0.002
Hydrogen Separation Vent	C	0.003^d	Flare	$60^c - 99^d$	0.00003 - 0.0012
Storage and Handling	D-G	0.57^d	Floating roof	85^d	0.086
			Vented to flare	99^d	0.00057
			Refrigerated vent condenser	80^d	0.114
Fugitive		0.11	Detection and correction	74^d	0.029
Secondary		0.067	None	---	0.067

[a] Emission factors are for a model plant with capacity 300 million kg per year. Actual emission factors may vary with throughput and control measures and should be determined through direct contacts with plant personnel. Factors are expressed as g benzene emitted per kg ethylbenzene/styrene produced.

[b] Source locations as shown in Figure 11.

[c] Reference 7.

[d] Reference 1.

Vacuum column vents remove air that leaks into the column, light hydrocarbons and hydrogen formed in dehydrogenation, non-combustibles in the column feed, and entrained aromatics. Most emissions occur on the benzene/toluene (B/T) column (B-2 in Figure 11). Uncontrolled distillation vents emit 4.2×10^{-3} kg HC per kg styrene in one plant where HC is benzene and toluene. Another condenser controlled vent emits 0.4×10^{-3} kg benzene/kg styrene.[2]

Following dehydrogenation, a hydrogen-rich gas (Stream 9 in Figure 11) containing methane, ethane, ethylene, carbon dioxide, carbon monoxide, and aromatics is normally cooled and compressed to recover aromatics. The stream should be vented to the atmosphere (Vent C) only during startup, shutdown, and during recovery section compressor outages. Some plants may also vent this stream to a flare. Flares are an efficient (99 percent) emission control only when flair diameter and gas flow are closely matched for optimum turbulence and mixing. They can be better controlled when the stream is routed to a manifold and burned with other fuels.

Stripper vents have been reported to emit 32 g ethylbenzene per kg styrene.[2] This corresponds to 9.6×10^{-3} g benzene per kg styrene. Benzene in shipping and storage (D-1 in Figure 11) must also be considered as a source if benzene is not produced on-site (in which case these emissions would be considered part of the benzene production process). Test data indicate an uncontrolled tank car/truck loading emission factor of 0.11 g/liter benzene, and an uncontrolled marine loading factor of 0.18 g/liter benzene.[2] Storage tank losses for floating-roof tanks can be estimated at 1.3×10^{-5} g/liter standing and 8.9×10^{-4} g/liter during withdrawal.[2] Other storage tanks (D-2, E, and F in Figure 11) are typically fixed-roof and have higher total emission rates but lesser benzene concentrations.

Emissions from Styrene Production Using Ethylbenzene Hydroperoxidation--

Only one United States facility currently reports using this method. Therefore, emission estimates are based on its capacity of 1200 million lbs/year styrene.

There are three main process emission sources: the ethylbenzene oxidation reactor vent (A in Figure 12), the propylene recycle purge vent (B), and the vacuum column vents (C) and (D). Propane vapor (B) is considered a fuel if it is not vented to the atmosphere. Of these sources, only the vacuum vents are large benzene emitters. This benzene results from benzene impurities in the ethylbenzene feed and minor side reactions in the process train.

The ethylbenzene oxidation reactor vent (A) releases carbon monoxide, light organics, entrained aromatics with nitrogen, oxygen, and carbon dioxide. The vent gas is scrubbed with oil and water for a 99 percent removal efficiency for organics. The resulting vent stream contains approximately 35 ppm benzene or 7.2 kg/hour.[7]

The propylene recycle vent (B) releases propane, propylene, ethane, and other impurities. No flow volume data are available but, based on a similar procedure in high-grade propylene production, this stream is a high-Btu gas and would be used as a fuel. No significant benzene emission is expected.[7]

The ethylbenzene hydroperoxidation process contains numerous vacuum columns and evaporators. Vents on these operations (C-1 - C-3) release inerts and light organics dissolved in the column feeds, nitrogen used for process pressure control, and entrained aromatics. A combined vent flow is reported to be 1.0×10^6 liters/hour containing about 27 kg/hour benzene.[7]

Other Sources of Emissions--

No specific information is available on storage, transport, or fugitive emissions for this process. The dehydrogenation vent (D) may be an emergency pressure vent similar to the separation vent (C in Figure 11).

Control methods for the two ethylbenzene/styrene processes in use in the United States include condensation, adsorption, flaring, and combustion in boilers or other process heaters. Controls for fugitive emissions from storage tanks, equipment leaks, and others include the use of floating-roof tanks and leak detection/correction programs. No information is available on control methods specific to the two processes mentioned in this report but not in use in the United States.

Condensers may be used to control benzene emissions associated with ethylbenzene/styrene production. The control efficiency of a condenser is determined by the temperature and pressure at which the condenser operates and by the concentration and vapor pressure of the organics in the vent stream. At typical pressures of 1 to 3 atmospheres and coil temperatures of 2 to 5°C, condensers can achieve 80 to 90 percent benzene reduction when used on vent streams at 70 to 100 percent saturation in benzene at 40 to 50°C.[7] Higher efficiencies become prohibitively expensive.

Condensers have limited use in handling high volume streams, short duration emergency releases, or cyclic releases such as the hydrogen separation vent. Furthermore, condensers are inefficient at low saturations such as with the alkylation reactor vents and the column vents of Figure 11.

In an ethylbenzene/styrene plant, a packed tower can be used to remove benzene. Polyethylbenzene (PEB) and various ethylbenzene produced during benzene alkylation are good absorbers of benzene and are normally recycled. This system is unsuitable, however, for handling high volume or intermittent releases of gases beyond the tower design capabilities. Absorption systems can maintain 80-99 percent benzene removal efficiencies for both saturated and unsaturated benzene streams depending on the tower design and operating variables.

Flare systems can control some streams for which condensation or absorption are not suitable. Flares can efficiently handle high saturated streams such as the alkylation vents. They can also control upset releases and other irregular releases, although the efficiency can be variable. The major difficulty here occurs in manifolding. High nitrogen or other low- or non-combustible gases may also be problematic. Consequently, there are no conclusive data on flare efficiency. Limited data show benzene destruction efficiencies ranging from 60 to 99 percent. A properly designed flare system must account for a range of flow and gas composition as well as the potential for explosion.

Use of vent gases as a fuel combined with regular process fuel is advantageous because vent flow variations can be better accounted for. Also, better gas/air mixing occurs along the entire flare front. As with flares, however, manifolding to ensure optimal combustion characteristics is the major technical problem. Process pressure variations and the possibility of emergency releases are complicating factors.

CYCLOHEXANE PRODUCTION

About 15 percent of the United States supply of benzene is used to produce cyclohexane.[9] Table 15 lists the location and current capacity for the United States cyclohexane producers. Of the nine plants, seven are located in Texas. One cyclohexane plant is located in Oklahoma and one in Puerto Rico. Two basic methods are used to produce cyclohexane: hydrogenation of benzene and petroleum liquid separation. About 85 percent of the cyclohexane produced domestically is produced through hydrogenation of benzene and the remainder is produced through separation of petroleum liquids. The following discussions of these two processes are taken from Reference 10.

Process Description: Benzene Hydrogenation

Figure 14 shows a model flow diagram for the manufacture of cyclohexane by benzene hydrogenation. High-purity benzene (Stream 1) is fed to the catalytic reactors in parallel and hydrogen (Stream 5) is fed into the reactors in series. Part of the cyclohexane separated in the flash separator is recycled (Stream 3) and fed to the reactors in series. Recycling helps to control the reactor temperature, since the reaction is

TABLE 15. UNITED STATES PRODUCERS OF CYCLOHEXANE[11,12]

Company	Location	Annual Capacity (10^6 gallons)
Chevron	Port Arthur, TX	38
E.I. duPont de Nemours and Company, Inc.	Corpus Christi, TX[a]	50
Phillips Petroleum Company		
Phillips 66 Company	Borger, TX Sweeny, TX[b]	45 111
Phillips Puerto Rico Core, Inc.	Guayama, PR	89
Sun Company, Inc.		
Sun Refining and Marketing Company	Tulsa, OK	>30
Texaco, Inc.		
Texaco Chemical Company	Port Arthur, TX	65
Union Pacific Corporation		
Champlin Petroleum Company	Corpus Christi, TX	22
Unocal Corporation		
Union Oil Company	Beaumont, TX	30
TOTAL		>480

[a] Plant closed July 1986.

[b] Plant closed mid-1986.

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel. These plant locations and capacities are current as of January 1, 1987.

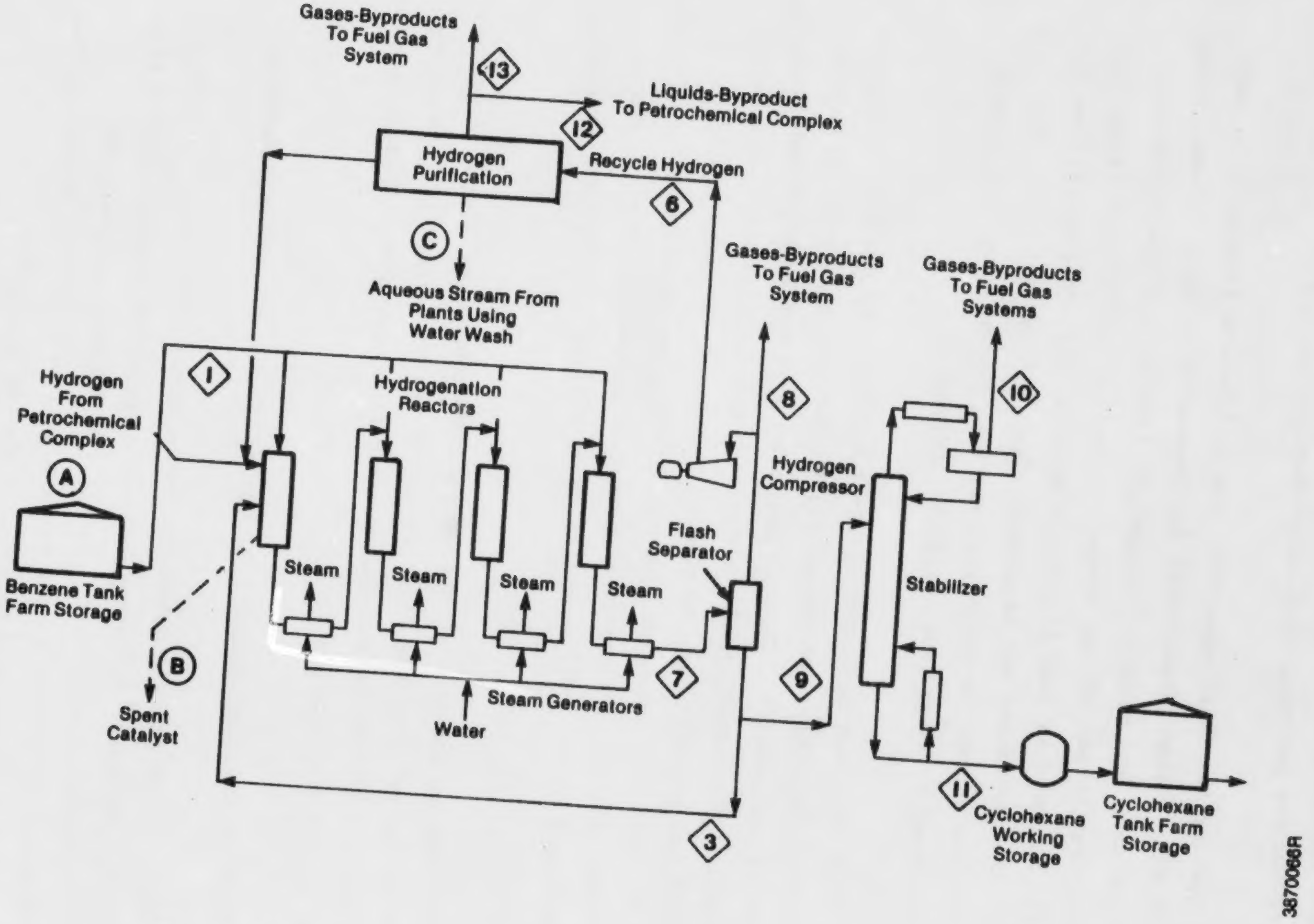

Gases-Byproducts To Fuel Gas System
13
Liquids-Byproduct To Petrochemical Complex
12
Hydrogen Purification
Recycle Hydrogen
6
C
Aqueous Stream From Plants Using Water Wash
Gases-Byproducts To Fuel Gas System
Gases-Byproducts To Fuel Gas Systems
Hydrogen From Petrochemical Complex
1
Hydrogenation Reactors
8
10
A
Hydrogen Compressor
Benzene Tank Farm Storage
Flash Separator
Steam
Steam
Steam
Steam
Stabilizer
B
Spent Catalyst
7
Steam Generators
Water
9
11
Cyclohexane Working Storage
Cyclohexane Tank Farm Storage
3
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Figure 14. Process Flow Diagram for Cyclohexane Production Using the Benzene Hydrogenation Process[10]

highly exothermic. The temperature is also controlled by generating steam, which is used elsewhere in the petrochemical complex. Both platinum and nickel catalysts are presently used to produce cyclohexane.

After leaving the flash separator, the cyclohexane (Stream 9) is sent to a distillation column (stabilizer) for removal of methane, ethane, other light hydrocarbons, and soluble hydrogen gas from the cyclohexane product. These impurities (Stream 10) are routed to the fuel-gas storage system for the facility and used as fuel in process heaters. Cyclohexane (Stream 11) purified in the stabilizer may be greater than 99.9 percent pure. The residual benzene content is typically less than 500 mg/liter. This pure product is stored in large tanks prior to shipment.

Gas from the flash separator, largely hydrogen, is not pure enough for direct reuse. Therefore, the stream (6) is purified before being recycled to (Stream 5) the reactor. Typical processes used for hydrogen purification are absorption and stripping of the hydrogen gas and cryogenic separation. Some plants use a combination of the two processes. Organic liquids (Stream 12) that are separated from the hydrogen in the hydrogen purification unit are sent to other petroleum processing units in the petrochemical complex. The separated gases (Stream 13) are used as fuel gas.

Depending on the type of hydrogen purification used, inert impurities present in the gas from the flash separator can be purged from the system before the gas enters the hydrogen purification equipment. This stream (8) is sent to the fuel gas system.

Benzene Emissions from Cyclohexane Production via Benzene Hydrogenation

There are no process emissions during normal operation.[10] During shutdowns, individual equipment vents are opened as required during final depressurization of equipment. Except for the feed streams, the concentration of benzene in the process equipment is low; therefore, few or no benzene emissions would be expected during a shutdown.[10]

Fugitive leaks can emit benzene or other hydrocarbons. Fugitive emissions from process pumps, valves, and compressors may also contain benzene. Storage of benzene (A in Figure 14) may also contribute to benzene emissions.

Other potential sources of emissions are catalyst handling (B) and absorber wastewater (C) (when an aqueous solution is used to purify the recycled hydrogen). Plants comprising at least 16 percent of the total cyclohexane capacity use an aqueous solution to purify hydrogen. Caution is taken to remove the organic from the spent catalyst before it is replaced. The spent catalyst is sold for metal recovery.[10]

Table 16 presents estimated emission factors for benzene emissions due to storage and fugitive emissions. The control technique applicable to storage facilities is the use of internal floating roof tanks.[10] The estimated efficiency of emission reduction is about 85 percent. For fugitive emissions, the control technique is an inspection/maintenance program, which can reduce emissions about 80 percent.

Process Description: Separation of Petroleum Fractions

Cyclohexane may also be produced by separation of select petroleum fractions. The process used to recovery cyclohexane in this manner is shown in Figure 15. A petroleum fraction rich in cyclohexane (Stream 1) is fed to a distillation column, in which benzene and methylcyclopentane are removed (Stream 2) and routed to a hydrogenation unit. The bottoms (Stream 3) from the column containing cyclohexane and other hydrocarbons are combined with another petroleum stream (4) and sent to a catalytic reformer, where the cyclohexane is converted to benzene. The hydrogen generated in this step may be used in the hydrogenation step or used elsewhere in the petrochemical complex.

The benzene-rich stream (5) leaving the catalytic reformer is sent to a distillation column, where compounds that have vapor pressure higher than benzene (pentanes, etc.) are moved (Stream 6) and used as by-products. The

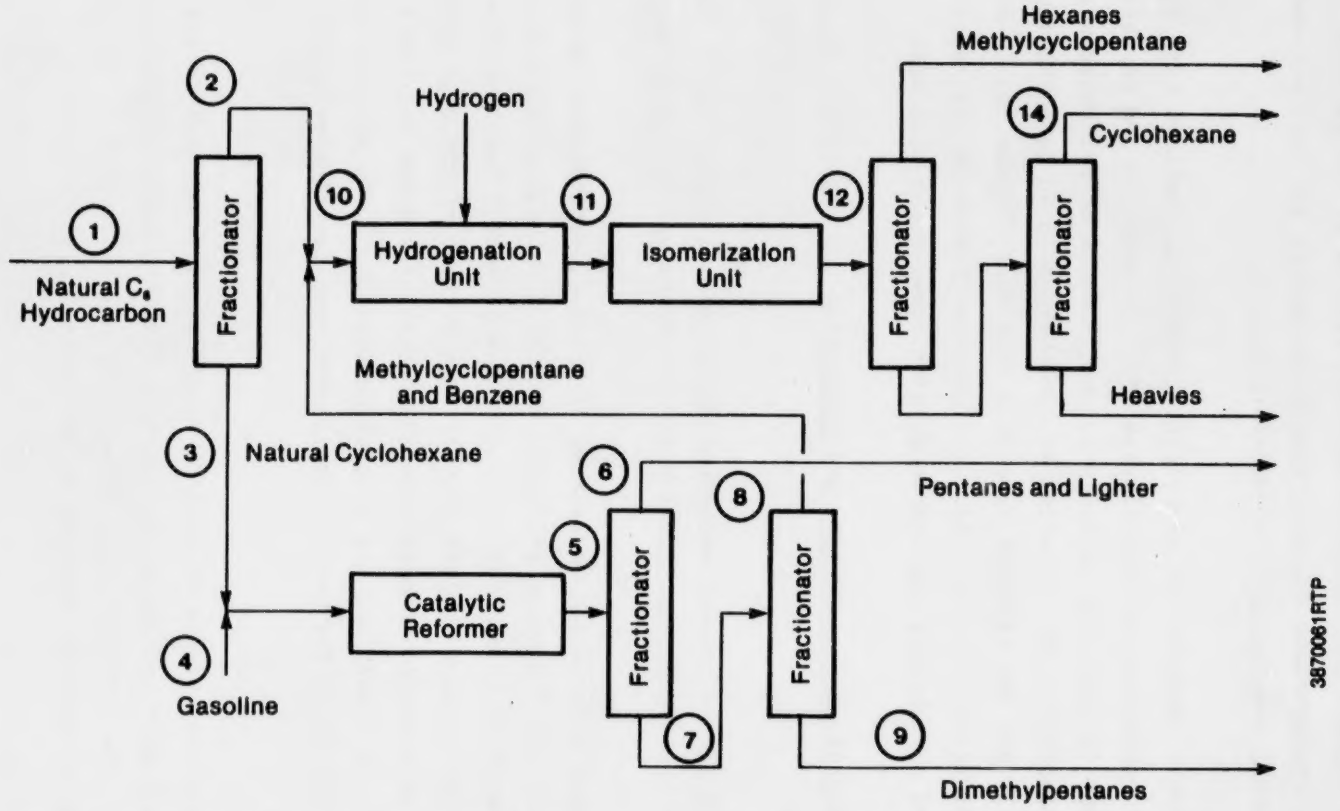
TABLE 16. ESTIMATED EMISSION FACTORS FOR BENZENE FROM CYCLOHEXANE PRODUCTION VIA BENZENE HYDROGENATION[10]

Source	Process Designation[a]	Uncontrolled Emissions g/Mg[b]	Controlled Emissions g/Mg[b]	Control Technique	Percent Efficiency
Benzene Storage	A	421	63.2	Internal floating roof tanks	85%
Process Fugitives	B	51.4	11.7	Inspection/ maintenance	80%

---

[a] Source locations refer to Figure 14.

[b] The emission factors are for hypothetical plants with an annual capacity of 150 Gg/yr. The reader is urged to contact specific facilities for information on processes and control techniques before applying these emission factors.


Hexanes
Methylcyclopentane
②
Hydrogen
⑭
Cyclohexane
①
⑩
⑪
⑫
Natural C_6 Hydrocarbon
Fractionator
Hydrogenation Unit
Isomerization Unit
Fractionator
Fractionator
Methylcyclopentane and Benzene
Heavies
③
Natural Cyclohexane
⑥
⑧
Pentanes and Lighter
⑤
Fractionator
Catalytic Reformer
Fractionator
④
Gasoline
⑦
⑨
Dimethylpentanes
3870061RTP

Note: Stream numbers correspond to the discussion in the text for this process.

Figure 15. Process Flow Diagram for Cyclohexane From Petroleum Fractions[10]

benzene-rich stream (7) that is left is sent to another distillation column, where the benzene and methylcyclopentane (Stream 8) are removed. The remaining hydrocarbons (largely dimethylpentanes) are used elsewhere in the petrochemical complex as by-products (Stream 9).

Stream 8 (benzene and methylcyclopentane) is combined with stream 2 and sent to a hydrogenation unit (Stream 10). Hydrogen is fed to this unit and the benzene is converted to cyclohexane. Isomers of cyclohexane such as methylcyclopentane are converted to cyclohexane in an isomerization unit (Stream 11) and the effluent from this equipment (Stream 12) is separated in a final distillation step. Pure cyclohexane (Stream 14) is separated from isomers of cyclohexane and compounds with lower vapor pressures.

Benzene Emissions from Cyclohexane Production via Separation of Petroleum Fractions

There are no process emissions during normal operation.[10] During emergency shutdowns, individual equipment vents are opened as required.

Equipment leaks can be sources of benzene, cyclohexane, methane, or other petroleum compounds emissions. Leaks from heat exchangers into cooling water or steam production can be a potential fugitive loss. Fugitive losses have special significance because of the high diffusivity of hydrogen at elevated temperatures and pressures and the extremely flammable nature of the liquid and gas processing streams.[10] No specific emission factors were found for benzene associated with fugitive emissions at these plants.

A potential source of benzene emissions is catalyst handling. Special efforts are made to remove the organics from the spent catalyst before it is replaced. The spent catalyst is sold for metal recovery.[10] No emission factors were found for benzene as related to catalyst handling.

CUMENE PRODUCTION

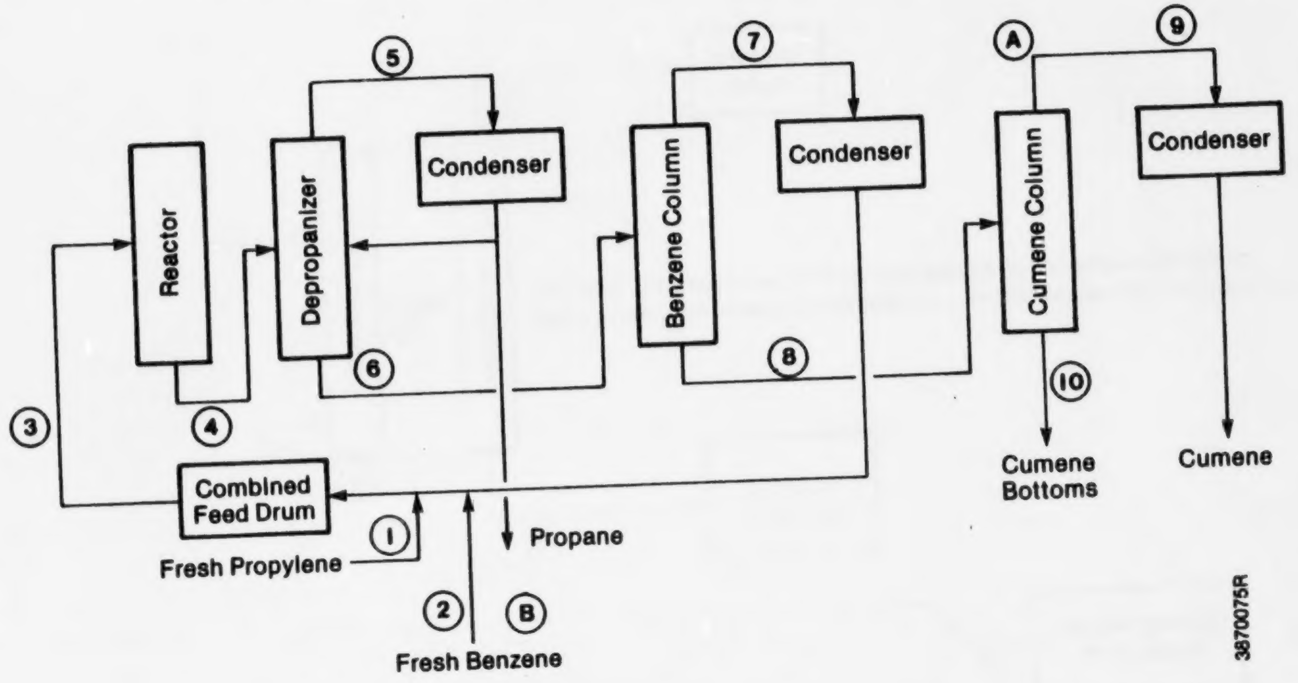
In the Unites States, cumene is produced by alkylating benzene with propylene. The location and capacities of United States producers of cumene are shown in Table 17. Benzene and propylene react at high temperatures and pressures in the presence of an acidic catalyst.[13] By far, the most common catalyst used is solid phosphoric acid. Figure 16 shows a process flow diagram for production of cumene using solid phosphoric acid as the catalyst. As shown in the figure, propylene and benzene are introduced into a pressurized combined feed drum (Streams 1 and 2). The feed ratio is usually 4 moles of benzene per mole of propylene.[13] From the feed drum, the benzene and propylene are sent to the reactor (Stream 3). From the reactor, the by-products, unreacted material, and product are separated by distillation. The depropanizer (Stream 4) removes propane, which is then sent through a condenser (Stream 5). Unpurified product is sent from the depropanizer to the benzene distillation column (Stream 6), where unreacted benzene is recovered and sent back to the combined feed drum (Stream 7). From the benzene column, the cumene product is sent to a cumene column (Stream 8), where the final product is separated (Stream 9) from residual bottoms (Stream 10). Residual bottoms may be burned as fuel or returned to a refinery for reforming.[13]

The production of cumene using an aluminum chloride process is similar to that using a solid phosphoric acid catalyst. The aluminum chloride method requires additional equipment to dry recycled streams and to neutralize reaction products. A simplified process flow diagram is shown in Figure 17. Aluminum chloride is a more reactive and less selective catalyst than solid phosphoric acid.[13] As shown in Figure 17, the propylene feed stock used in this process must be dried and treated to remove organic sulfur compounds. The benzene must also be dried. Benzene and propylene are sent to a catalyst mix tank (Streams 1 and 2), where aluminum chloride powder is added to form the catalyst complex (Stream 4). Hydrogen chloride gas is added to activate the catalyst (Stream 5). The resulting catalyst suspension (Stream 6) and fresh benzene (Stream 7) are fed into the

TABLE 17. UNITED STATES PRODUCERS OF CUMENE AND ANNUAL CAPACITY[11]

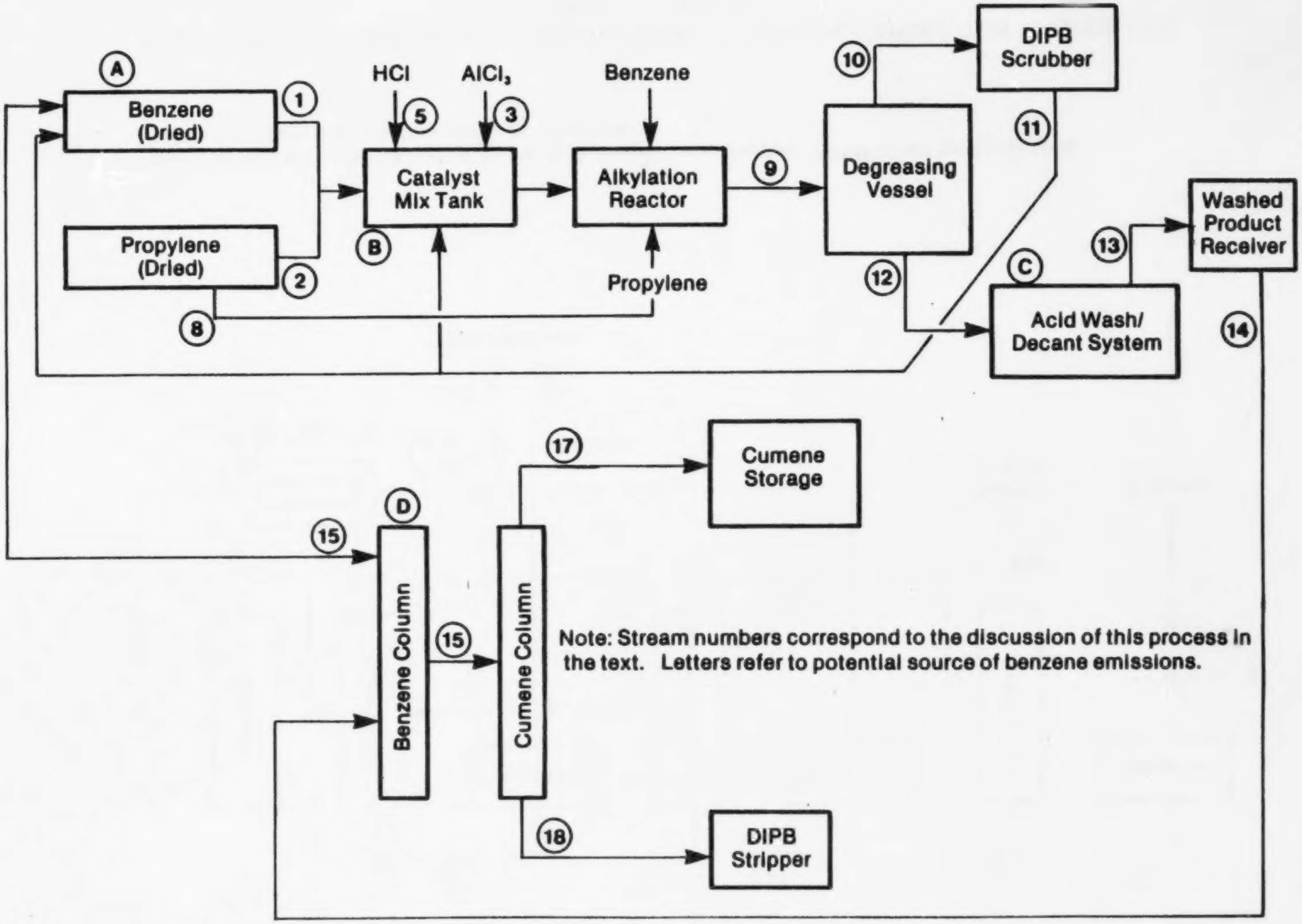
Plant	Location	Annual Capacity (10^6 lb)	Notes
Amoco Chemicals Company	Texas City, TX	30	Captive for methylstyrene
Ashland Chemical Company	Catlettsburg, KY	400	Cumene is sold
BTL Specialty Resins Corporation	Blue Island, IL	110	Captive for phenol
Champlin Petroleum Company	Corpus Christi, TX	450	---
Chevron Chemical Company	Philadelphia, PA	450	Cumene is sold
	Port Arthur, TX	450	Cumene is sold
Coastal States Marketing	Westville, NJ	140	Cumene is sold
Georgia Gulf Corporation	Pasadena, TX	750	Some cumene transferred to company's phenol/acetone plant
Koch Refining Company	Corpus Christi, TX	550	Cumene is sold
Shell Chemical Company	Deer Park, TX	900	Captive for phenol/acetone
Texaco Chemical Company	El Dorado, KS	135	Captive for phenol/acetone

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel. These locations, producers, and capacities are as of January 1987.


⑤
⑦
Ⓐ
⑨
Reactor
Depropanizer
Condenser
Benzene Column
Condenser
Cumene Column
Condenser
⑥
⑧
③
④
⑩
Combined Feed Drum
Cumene Bottoms
Cumene
①
Fresh Propylene
Propane
②
Ⓑ
Fresh Benzene
3870075R

Note: The Stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene.

Figure 16. Process for the Manufacture of Cumene Using Solid Phosphoric Acid Catalyst[13]


Ⓐ
Benzene (Dried)
①
Propylene (Dried)
②
⑧
HCl
⑤
AlCl$_3$
③
Catalyst Mix Tank
Ⓑ
Benzene
Alkylation Reactor
Propylene
⑨
⑩
Degreasing Vessel
⑫
DIPB Scrubber
⑪
Ⓒ
Acid Wash/ Decant System
⑬
Washed Product Receiver
⑭
⑮
Ⓓ
Benzene Column
⑮
Cumene Column
⑰
Cumene Storage
⑱
DIPB Stripper
3870065R

Note: Stream numbers correspond to the discussion of this process in the text. Letters refer to potential source of benzene emissions.

Figure 17. Simplified Process Flow Diagram for Cumene Production Using Aluminum Chloride Catalyst[13]

alkylation reactor and propylene is introduced into the bottom of the reactor (Stream 8). The crude reaction mixture is then fed to a degassing vessel (Stream 9), where hydrocarbons such as propane are released from solution. This vapor stream is scrubbed with a weak caustic solution. The washed hydrocarbon vapor is recontacted with diisopropylbenzene (DIPB) in the DIPB scrubber (Stream 10) to extract residual unreacted propylene.[13] Then, the stream containing the propylene is sent back to the catalyst mix tank (Stream 11).

The product from the alkylation reactor is forwarded to an acid wash tank where the catalyst complex is broken down. A resulting hydrocarbon-water mixture is sent through a series of decanters (Stream 12) and the decanted hydrocarbon layer is stored in a washed product receiver tank (Stream 13). The wash/decanter system is blanketed with nitrogen.

The crude product from the washed product receiver (Stream 14) tank is sent to the benzene recovery column to strip excess benzene. Any benzene recovered is returned to the benzene feed tank (Stream 15). Crude cumene product is then distilled (Stream 16).

The cumene distillation column and receiver tank are blanketed with nitrogen to protect the cumene from air. Cumene product is then sent to storage (Stream 17). The bottoms from the cumene distillation column (Stream 18) contain crude DIPB, some cumene, alkylbenzenes, and miscellaneous tars.[13] The bottoms stream is sent to a DIPB stripper and DIPB is eventually returned to the alkylation reactor.[13]

Benzene Emissions from Cumene Production

In the solid phosphoric acid process, the cumene column vent (A in Figure 16) is a potential source of benzene emissions. The system operates at a pressure slightly higher than atmospheric pressure to make sure than no air contacts the cumene product.[13] Methane is used to pressurize the system. This methane is eventually vented carrying with it other hydrocarbon vapors.[13] No specific emission factors were found for benzene emissions from the cumene column. One factor for total VOC emissions indicated that 0.03 g VOC were emitted per kg cumene produced and that benzene constituted a "trace amount" of the hydrocarbons in the stream.[13]

Emissions of benzene from the production of cumene using an aluminum chloride catalyst are associated with the benzene azeotropic drying column (A in Figure 17), the scrubber or the catalyst mix tank (B), the wash decanter system (C), and the benzene recovery column (D).[13] No specific emission factors were found for benzene emissions from these sources. However, one reference provided VOC emission factoring and estimated percent composition of the emissions.[13] Table 18 presents these data. The percent (weight) of benzene may be used along with a cumene production volume to estimate benzene emissions from these sources. The control technique most applicable to these sources is flaring, with an estimated efficiency of 95 percent.[13]

PHENOL PRODUCTION

Over 90 percent of the phenol produced in the United States is based on peroxidation of cumene.[14] Table 19 shows the locations, capabilities, and production methods of the phenol producers in the United States. Because benzene may be present in the cumene feedstock, benzene may be emitted during production of phenol.

A flow diagram for the production of phenol via cumene peroxidation is shown in Figure 18. The process essentially involves two steps. First, air is introduced into an emulsion of purified cumene to produce cumene hydroperoxide (Stream 1). Then, dilute sulfuric acid is added to cleave the compound directly into phenol and acetone. The acetone are separated (Stream 3) by distillation and phenol is recovered from the finishing column (Stream 4).[14]

TABLE 18. VOC EMISSIONS AND WEIGHT PERCENT BENZENE FOR HYPOTHETICAL PLANT PRODUCING CUMENE BY PROCESS USING ALUMINUM CHLORIDE CATALYST[13]

Emission Source	Stream Designation[a]	Uncontrolled VOC Emissions Factor[b] g/Kg	Uncontrolled VOC Emissions Factor[b] Wt% Benzene	Controlled VOC Emission Factor[b] g/Kg	Control Device	VOC Emission Reduction (%)
Benzene Azeotrope Drying Column	A	0.02	100	0.001	Flare	95
Catalyst Mix Tank Scrubber	B	0.16	99.4	0.008	Flare	95
Wash-Decanter System	C	0.01	78.4	0.0005	Flare	95
Benzene Recovery Column	D	0.017	100	0.00085	Flare	95

[a] Stream designations refer to Figure 18.

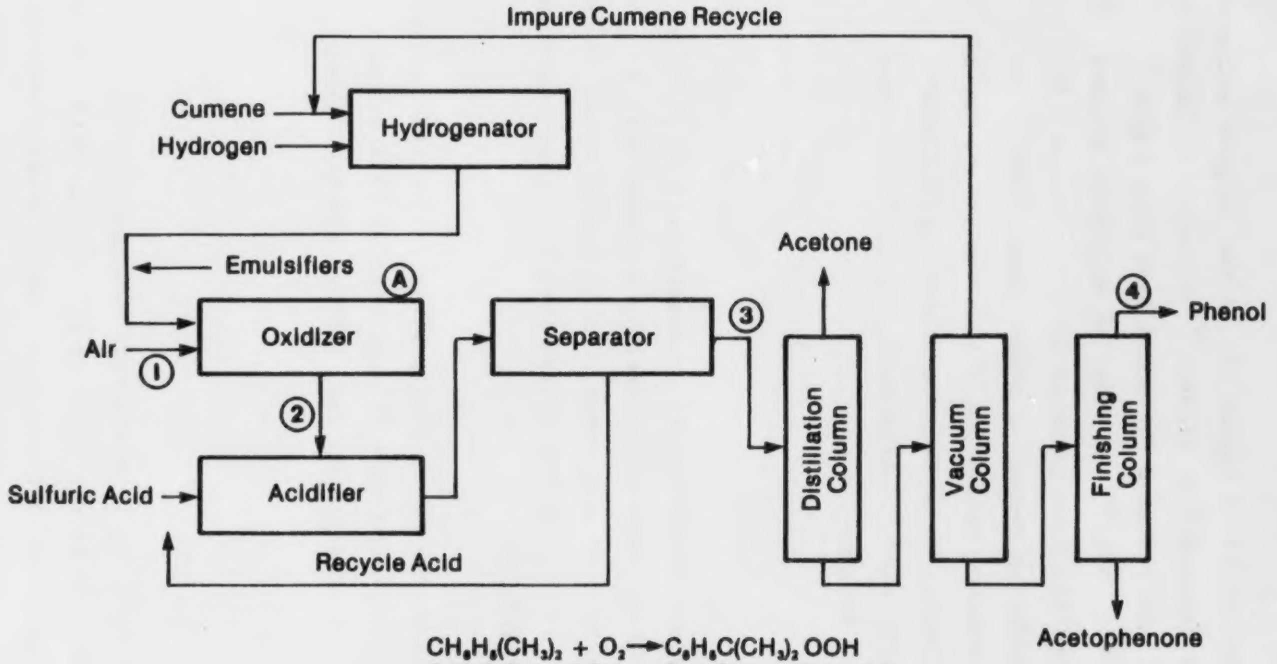
[b] Factors are expressed as grams of VOC per Kg cumene produced.

Note: These emission factors are estimates, based on a hypothetical plant producing 227 Gg cumene per year. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and type of control device used at a particular facility before applying these emission factors.

TABLE 19. UNITED STATES PRODUCERS OF PHENOL, THEIR LOCATIONS AND CAPACITIES[11]

Facility	Location	Annual Capacity (Millions of Pounds)	Process and Raw Material
Allied-Signal, Inc. Allied Corporation, Chemical Sector	Frankford, PA	550	Cumene peroxidation
Aristech Chemical Corporation	Haverhill, OH	600	Cumene peroxidation
BTL Specialty Resins Corporation	Blue Island, IL	88	Cumene peroxidation
Dow Chemical U.S.A.	Oyster Creek, TX	460	Cumene peroxidation
General Electric Company Plastics Business Operations	Mount Vernon, IN	400	Cumene peroxidation
Georgia Gulf Corporation	Bound Brook, NJ	157	Cumene peroxidation
	Plaquemine, LA	360	Cumene peroxidation
Kalama Chemical, Inc.	Kalama, WA	60	Toluene oxidation
Merichem Company	Houston, TX	35	Petroleum and coal tar
PMC, Inc.	Santa Fe Springs, CA	8	Petroleum and coal tar
Shell Oil Company Shell Chemical Company, division	Deer Park, TX	545	Cumene peroxidation
Stimson Lumber Company Northwest Petrochemical Corporation, division	Anacortes, WA	<5	Petroleum
Texaco, Inc. Texaco Chemical Company, subsidiary	El Dorado, KS	95	Cumene peroxidation
TOTAL		<3398	

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. These data on producers and locations are as of January 1987.


Impure Cumene Recycle
Cumene
Hydrogen
Hydrogenator
Emulsifiers
Ⓐ
Air
①
Oxidizer
②
Sulfuric Acid
Acidifier
Recycle Acid
Separator
③
Acetone
Distillation Column
Vacuum Column
Finishing Column
④
Phenol
Acetophenone

$CH_6H_5(CH_3)_2 + O_2 \rightarrow C_6H_5C(CH_3)_2OOH$
$C_6H_5C(CH_3)_2OOH \rightarrow C_6H_5OH + (CH_3)_2CO$

3870076R

Note: Stream numbers correspond to the discussion of this process in the text.
Letters refer to potential sources of benzene emissions.

Figure 18. Flow Diagram for the Manufacture of Phenol by the Cumene Peroxidation Process[14]

Benzene Emissions from Phenol Production

"Spent air" from the oxidizer (A in Figure 18) is the largest source of benzene emissions at cumene-process phenol plants.[14] An emission factor of 2×10^{-6} kg benzene/kg phenol was reported for one source from a post oxidizer concentration condenser vent.[14] An order of magnitude estimate of 1.0×10^{-3} kg benzene/kg phenol has been reported in the literature for plants using the cumene peroxidation method of phenol production.[15] No details were given in the literature concerning the derivation of any of these emission factors. The reader is urged to contact specific plants to obtain information on emissions, control techniques, and processes used before applying these emission factors.

NITROBENZENE PRODUCTION

Benzene is a major feedstock in commercial processes used to produce nitrobenzene. In these processes, benzene is directly nitrated with a mixture of nitric acid, sulfuric acid, and water. As of January 1986, four companies were producing nitrobenzene in the United States. Their names and plant locations are shown in Table 20.

A discussion of the nitrobenzene production process, potential sources of benzene emissions, and control techniques is presented in this section. Unless otherwise referenced, the information that follows has been taken directly from Reference 13.

Process Descriptions

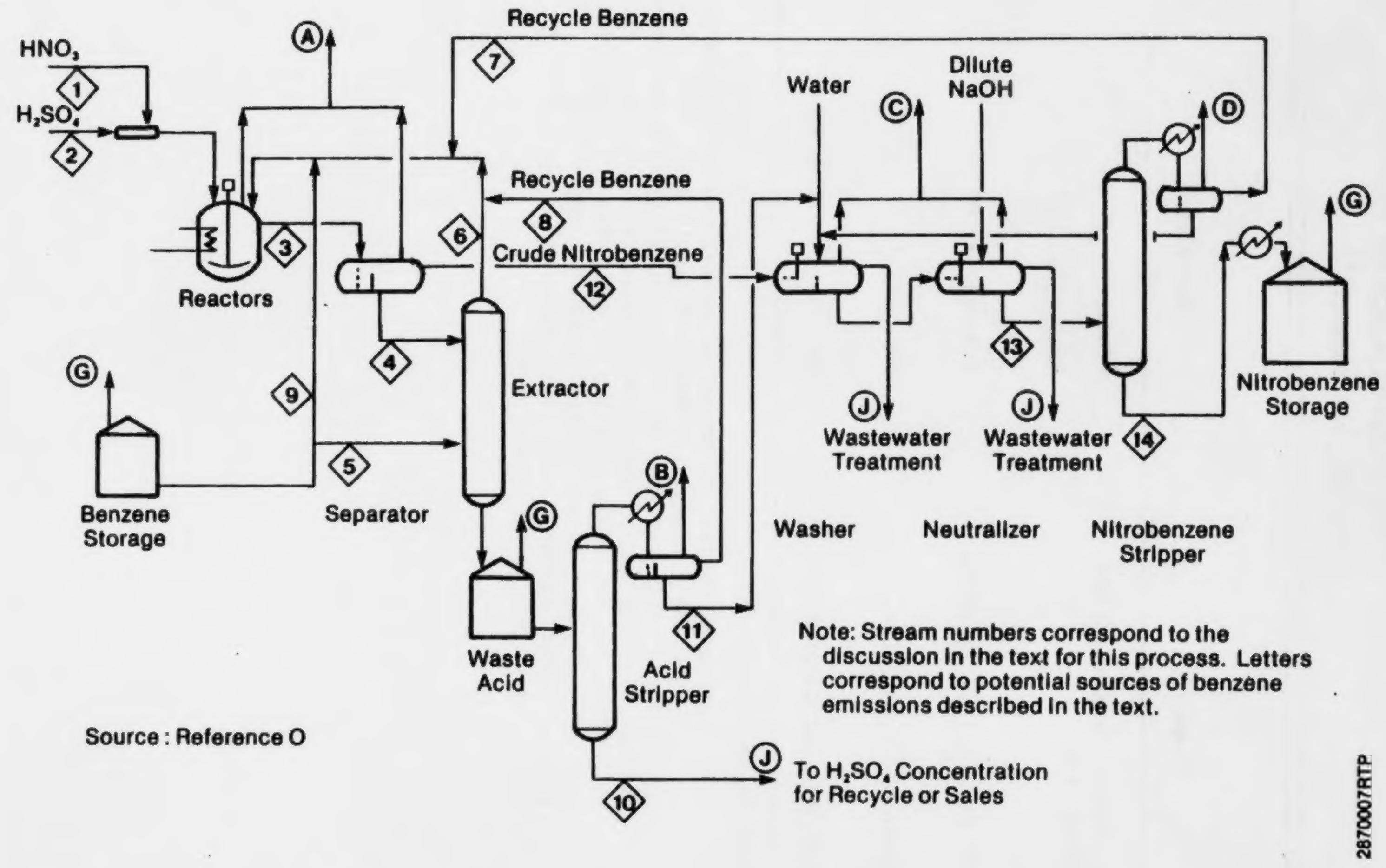
Nitrobenzene is produced by a highly exothermic reaction in which benzene is reacted with nitric acid in the presence of sulfuric acid. Most commercial plants use a continuous nitration process, where benzene and the acids are mixed in a series of continuous stirred-tank reactors.[16] A flow diagram of the basic continuous process is shown in Figure 19.

TABLE 20. UNITED STATES NITROBENZENE PRODUCERS, LOCATIONS, AND CAPACITY[11]

Company	Location	Annual Capacity (10^6 lbs)
E.I. duPont de Nemours and Company, Inc.	Beaumont, TX	350
	Gibbstown, NJ[a]	240
First Chemical Corporation	Pascagoula, MS	300
Rubicon Chemicals, Inc.	Geismar, LA	427
Mobay Chemical Corporation	New Martinsville, WV	190

[a] Plant is on standby.

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. These data on producers and location are as of January 1987.


Recycle Benzene
HNO$_3$
1
H$_2$SO$_4$
2
A
7
Water
C
Dilute NaOH
D
G
Recycle Benzene
8
3
6
Crude Nitrobenzene
12
Reactors
4
13
G
9
Extractor
J
J
Nitrobenzene Storage
Wastewater Treatment
Wastewater Treatment
14
5
B
Benzene Storage
Separator
G
Washer
Neutralizer
Nitrobenzene Stripper
11
Waste Acid
Acid Stripper
J
To H$_2$SO$_4$ Concentration for Recycle or Sales
10
2870007RTP

Source : Reference O

Note: Stream numbers correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions described in the text.

Figure 19. Process Flow Diagram for Manufacture of Nitrobenzene[13]

As shown in the figure, nitric acid (Stream 1) and sulfuric acid (Stream 2) are mixed before flowing into the reactor. Benzene extract (Stream 6), two recovered and recycled benzene streams (Streams 7 and 8), and as much additional benzene (Stream 9) as is required make up the benzene charge to the reactor.

For the process depicted here, nitration occurs at 55°C under atmospheric pressure. Cooling coils are used to remove the heat generated by the reaction. There is evidence to suggest that other methods/conditions may also be used in the continuous nitration process.[17] It is not known whether these processes are currently in use.

Following nitration, the crude reaction mixture (Stream 3) flows to the decanter, where the organic phase of crude nitrobenzene is separated from the aqueous waste acid. The crude nitrobenzene (Stream 12) subsequently flows to the washer and neutralizer, where mineral (inorganic) and organic acids are removed. The washer and neutralizer effluents are discharged to wastewater treatment. The organic layer (Stream 13) is fed to the nitrobenzene stripper, where water and most of the benzene and other low boilers are carried overhead. The organic phase carried overhead is primarily benzene and is recycled (Stream 7) to the reactor. The aqueous phase (carried overhead) is sent to the washer. Stripped nitrobenzene (Stream 14) is cooled and then transferred to nitrobenzene storage.

The treatment, recycling, or discharge of process streams are also shown in the flow diagram. Aqueous waste acid (Stream 4) from the decanter flows to the extractor, where it is denitrated. There, the acid is treated with fresh benzene from storage (Stream 5) to extract most of the dissolved nitrobenzene and nitric acid. The benzene extract (Stream 6) flows back to the nitrating reactor, whereas the denitrated acid is stored in the waste acid tank.

Benzene is commonly recovered from the waste acid by distillation in the acid stripper. The benzene recovered is recycled (Stream 8) and water carried overhead with the benzene is forwarded (Stream 11) to the washer.

The stripped acid (Stream 10) is usually reconcentrated on-site but may be sold.[13]

Typically, many of the process steps are padded with nitrogen gas to reduce the chances of fire or explosion. This nitrogen padding gas and other inert gases are purged from vents associated with the reactor and separator (Vent A in Figure 19), the condenser on the acid stripper (Vent B), the washer and neutralizer (Vent C), and the condenser on the nitrobenzene stripper (Vent D).

Benzene Emissions from Nitrobenzene Production

Benzene emissions may occur at numerous points during the manufacture of nitrobenzene. These emissions may be divided into four types: process emissions, storage emissions, fugitive emissions, and secondary emissions.

Process emissions occur at the following four gas-purge vents: (1) the reactor and separator vent, (2) the acid stripper vent, (3) the washer and neutralizer vent, (3) the washer and neutralizer vent, and (4) the nitrobenzene stripper vent. The bulk of benzene emissions occur from the reactor and separator vent. This vent releases about 3 times the level of benzene released from Vents B and D (Figure 19), and about 120 times that released from Vent C. For all these vents, the majority of VOC emissions is in the form of benzene. Benzene accounts for 99, 100, 76, and 99 percent of total VOC emissions from Vents A, B, C, and D, respectively. Table 21 shows estimated emission factors for benzene from these sources.

Other emissions include storage, fugitive, and secondary emissions. Storage emissions (G) occur from tanks storing benzene, waste acid, and nitrobenzene. Fugitive emissions of benzene can occur when leaks develop in valves, pump seals, and other equipment. Leaks can also occur from corrosion by the sulfuric and nitric acids and hinder control of fugitive emissions.

TABLE 21. UNCONTROLLED AND CONTROLLED BENZENE EMISSION FACTORS FOR HYPOTHETICAL NITROBENZENE PRODUCTION PLANTS[13]

Source	Stream Designation[a]	Uncontrolled Emission Factor g/kg[b]	Controlled Control Device or Technique	Controlled Emission Reduction (%)	Controlled Emission Factor g/kg[b]
		For 90,000 Mg/yr Capacity Plant			
Reactor and separator	A	0.960	---	---	---
Waste-acid stripper	B	0.170	---	---	---
Wash and neutralization	C	0.0081	Vent absorber	94.6	0.0776
Nitrobenzene stripper	D	0.170	Thermal oxidizer	99.0	0.0144
Small benzene storage[d]	G	0.078	---	---	---
Waste-acid storage[d]	G	0.051	---	---	---
Benzene storage[d]	G	0.283	Internal floating roof	85	0.0425
Fugitive[c]	H	0.63	Detect and correct minor leaks plus mechanical seals	67.7	0.165
Secondary	J	0.10	None	---	0.10
Total with vent absorber		2.45	---	---	0.39
Total with thermal oxidizer		2.45	---	---	0.22
		For 150,000 Mg/yr Capacity Plant			
Reactor and separator	A	0.960	---	---	---
Waste-acid stripper	B	0.170	---	---	---
Wash and neutralization	C	0.0081	Vent absorber	94.6	0.0774
Nitrobenzene stripper	D	0.170	Thermal oxidizer	99.0	0.0143
Small benzene storage[d]	G	0.077	---	---	---
Waste-acid storage[d]	G	0.048	---	---	---

TABLE 21. UNCONTROLLED AND CONTROLLED BENZENE EMISSION FACTORS FOR HYPOTHETICAL NITROBENZENE PRODUCTION PLANTS[13] (Continued)

Source	Stream Designation[a]	Uncontrolled	Controlled		
		Emission Factor g/kg[b]	Control Device or Technique	Emission Reduction (%)	Emission Factor g/kg[b]
Benzene storage[d]	G	0.281	Floating roof	85	0.0421
Fugitive[c]	H	0.38	Detect and correct leaks plus mechanical seals	67.7	0.099
Secondary	J	0.10	None	---	0.10
Total with vent absorber		2.19	---	---	0.32
Total with thermal oxidizer		2.19	---	---	0.26

[a] Stream designations refer to Figure 19.

[b] Factors are expressed as grams of benzene emitted per kg nitrobenzene produced.

[c] Process pumps and valves are potential sources of fugitive emissions. Each model plant is estimated to have 42 pumps (including 17 spares), 500 process valves, and 20 pressure-relief valves based on data from an existing facility. All pumps have mechanical seals. Twenty-five percent of these pumps and valves are being used in benzene service. The fugitive emissions included in this table are based on the factors given in Appendix A.

[d] Storage emission factors are based on these tank parameters:

	For 90,000 Mg/yr Model Plant		
	Tank Size	Turnovers/ Year	Bulk Liquid Temperature °C
Benzene (large tank)	2,840	24	20
Benzene (small tank)	284	236	20

	For 150,000 Mg/yr Model Plant		
	Tank Size	Turnovers/ Year	Bulk Liquid Temperature °C
Benzene (large tank)	4,730	24	20
Benzene (small tank)	473	236	20

Secondary emissions can result from the handling and disposal of process waste liquid. Three potential sources of benzene storage emissions (J) are the wastewater from the nitrobenzene washer, waste caustic from the nitrobenzene neutralizer, and waste acid from the acid stripper. Where waste acid is not stripped before its sale or reconcentration, secondary emissions would be significantly affected (increased), unless the reconcentration process is adequately controlled.

Table 21 gives benzene emission factors before and after the application of possible controls for two hypothetical plants using the continuous nitration process. The two plants differ in their plant capacities; one plant produces 90,000 Mg/yr and the other produces 150,000 Mg/yr or nitrobenzene. Both plants use a vent absorber or thermal oxidizer to control process emissions in conjunction with waste-acid storage and small benzene storage emissions. The values presented for the main benzene storage emissions were calculated by assuming that a contact-type internal floating roof with secondary seals will reduce fixed-roof-tank emissions by 85 percent. The values presented for controlled fugitive emissions are based on the assumption that leaks from valves and pumps, resulting in concentrations greater than 10,000 ppm on a volume basis, are detected and that appropriate measures are taken to correct the leaks. Secondary emissions and nitrobenzene storage emissions are assumed to be uncontrolled. Uncontrolled emission factors are based on the assumptions given in footnotes to Table 21. The controlled emission rates from these hypothetical plants range from 0.22 kg/Mg to 0.39 kg/Mg. Actual emissions from nitrobenzene plants would be expected to vary, depending on process variations, operating conditions, and control methods.

A variety of control devices may be used to reduce emissions during nitrobenzene production, but insufficient information is available to determine which devices nitrobenzene producers are using currently. Process emissions may be reduced by vent absorbers, water scrubbers, condensers, incinerators, and/or thermal oxidizers. Storage emissions from the waste-acid storage tank and the small benzene storage tank can be readily controlled in conjunction with the process emissions. (A small storage tank contains approximately one day's supply of benzene; the larger tank is the main benzene storage tank.) In contrast, emissions from the main benzene storage tanks are controlled by using floating-roof storage tanks. Fugitive emissions are generally controlled by detecting and correcting leaks, whereas, secondary emissions are generally uncontrolled.

ANILINE PRODUCTION

Almost 97 percent of the nitrobenzene produced in the United States is converted to aniline.[13] Because of its presence as an impurity in nitrobenzene, emissions of benzene may occur during aniline production. Therefore, a brief discussion of the production of aniline from nitrobenzene and its associated benzene emissions is included in this report. Table 22 lists the United States producers of aniline and the production method. A process flow diagram is shown in Figure 20. As shown in the figure, nitrobenzene (Stream 1) is vaporized and fed with excess hydrogen (Stream 2) to a fluidized bed reactor. The product gases (Stream 3) are passed through a condenser. The condensed materials are decanted (Stream 4) and non-condensible materials are recycled to the reactor (Stream 5). In the decanter, one phase (Stream 6) is crude aniline and the other is an aqueous phase (Stream 7). The crude aniline phase is sent to a dehydration column that operates under vacuum. Aniline is recovered from the aqueous phase by stripping or extraction with nitrobenzene. Overheads from the dehydration column (Stream 8) are condensed and recycled to the decanter. The bottoms from the dehydration column, which contain aniline, are sent to the purification column. Overheads (Stream 10) from the purification column contain the aniline product, while the bottoms (Stream 11) contain tars.[13]

Benzene Emissions from Aniline Production

Process emissions of benzene typically originate from the purging of non-condensibles during recycle to the reactor and purging of inert gases from separation and purification equipment (A in Figure 20).[14]

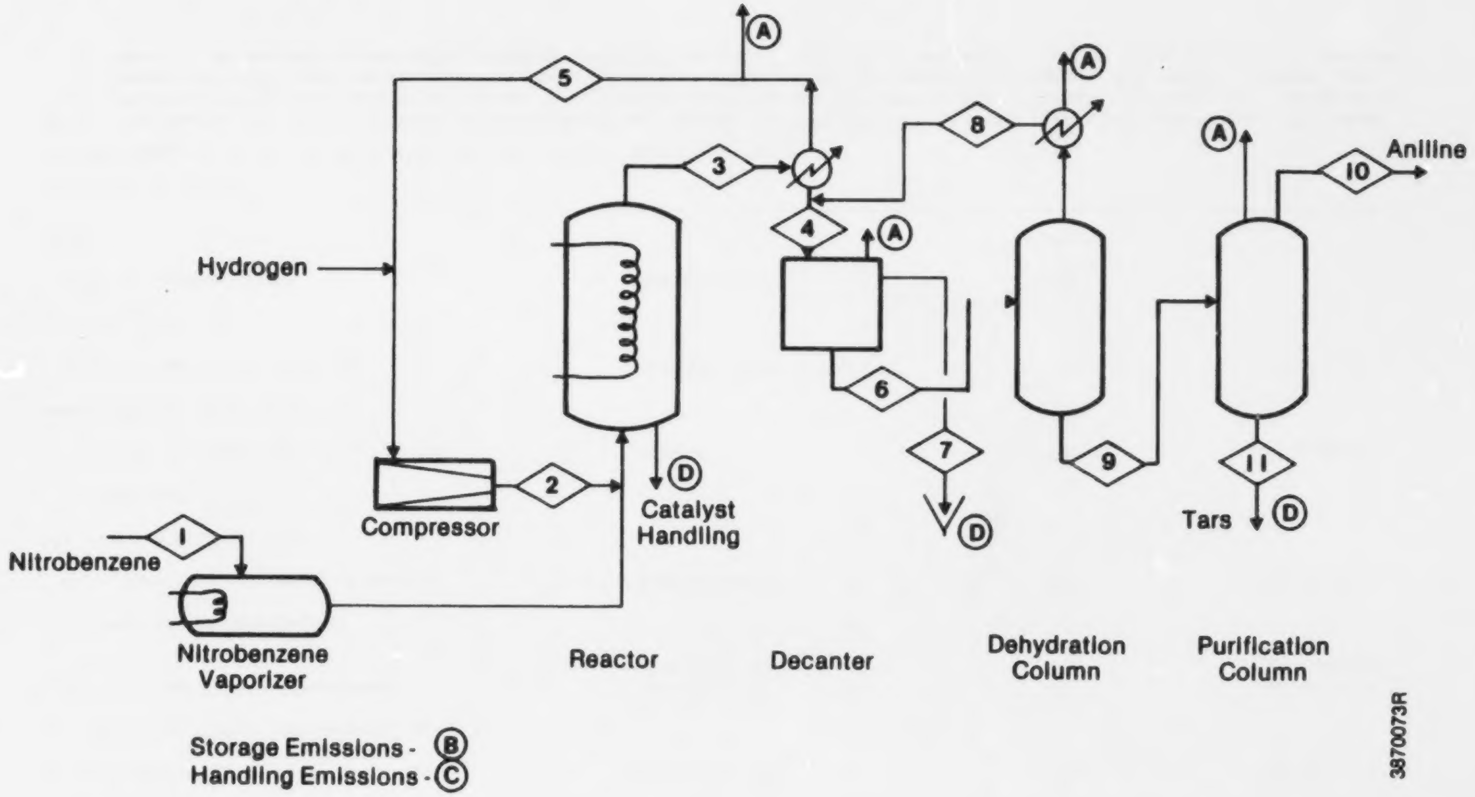
TABLE 22. UNITED STATES PRODUCERS OF ANILINE, THEIR LOCATIONS AND CAPACITIES[11]

Facility	Location	Annual Capacity (Millions of Pounds)	Raw Material and Remarks
Aristech Chemical Corporation	Haverhill, OH	200	Phenol
E.I. duPont de Nemours and Company, Inc.			
Chemicals and Pigments Department	Beaumont, TX	260	Nitrobenzene
	Gibbstown, NJ	170[a]	Nitrobenzene
First Mississippi Corporation			
First Chemical Corporation, subsidiary	Pascagoula, MS	250	Nitrobenzene
ICI American Holdings, Inc.			
ICI Americas, Inc.			
Rubicon Chemicals, Inc.	Geismar, LA	320	ICI process
Mobay Chemical Corporation			
Inorganic Chemicals Division	New Martinsville, WV	42	Iron oxides
Uniroyal, Inc.			
Uniroyal Chemical Group	Geismar, LA	[b]	
TOTAL		1242	

[a] Plant is on standby.

[b] Jointly operated by Rubicon Chemicals, Inc. and Uniroyal Chemical Group.

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. These data on producers and locations are as of January 1987.


A
5
A
8
A
3
A
10
Aniline
4
A
Hydrogen
6
7
9
11
D
Catalyst Handling
Tars
D
D
2
Compressor
1
Nitrobenzene
Nitrobenzene Vaporizer
Reactor
Decanter
Dehydration Column
Purification Column
3870073R
Storage Emissions - B
Handling Emissions - C

Note: Stream numbers correspond to the discussion in the text for this process.
Letters correspond to emission sources of benzene.

Figure 20. Flow Diagram for Manufacture of Aniline[13]

Only one emission factor was found for benzene emissions from aniline production. For process vents (A), an uncontrolled emission factor of 0.0057 kg benzene/Mg aniline produced was reported in the literature.[13] No details of its derivation were provided, other than it was based on data provided by an aniline producer.

Control techniques available for emissions associated with the purging of equipment vents include water scrubbing and thermal oxidation.[13] No data were found to indicate the efficiencies of these control devices for benzene emissions. The reader is urged to contact specific production facilities before applying the emission factor given in this report to determine exact process conditions and control techniques.

CHLOROBENZENE PRODUCTION

Of the chlorobenzenes, mono-, di-, and trichlorobenzene have important industrial applications.[18] Therefore, this section of the report focuses on benzene emissions associated with production of these three types of chlorobenzenes. Table 23 lists the producers of mono-, di-, and trichlorobenzene in the United States. The producing companies' capabilities are flexible such that different chlorobenzenes may be isolated, depending on market demand. Di- and trichlorobenzenes are produced in connection with monochlorobenzene. The relative amounts of the products can be varied by process control.[19] Figure 21 shows a process flow diagram for the manufacture of mono-, di-, and trichlorobenzenes.

The benzene is dried and then transferred to the dry benzene feed tank (Stream 1). Chlorine is also moved from storage to the feed tank (Stream 2). The dry benzene is reacted with the gaseous chlorine in the presence of an iron turning catalyst (Stream 3). The quantity of chlorine added to the reactors determines the product distribution. Hydrogen chloride is generated through the chlorination reaction. This material is sent to the hydrogen chloride scrubber (Stream 4), where it is scrubbed with

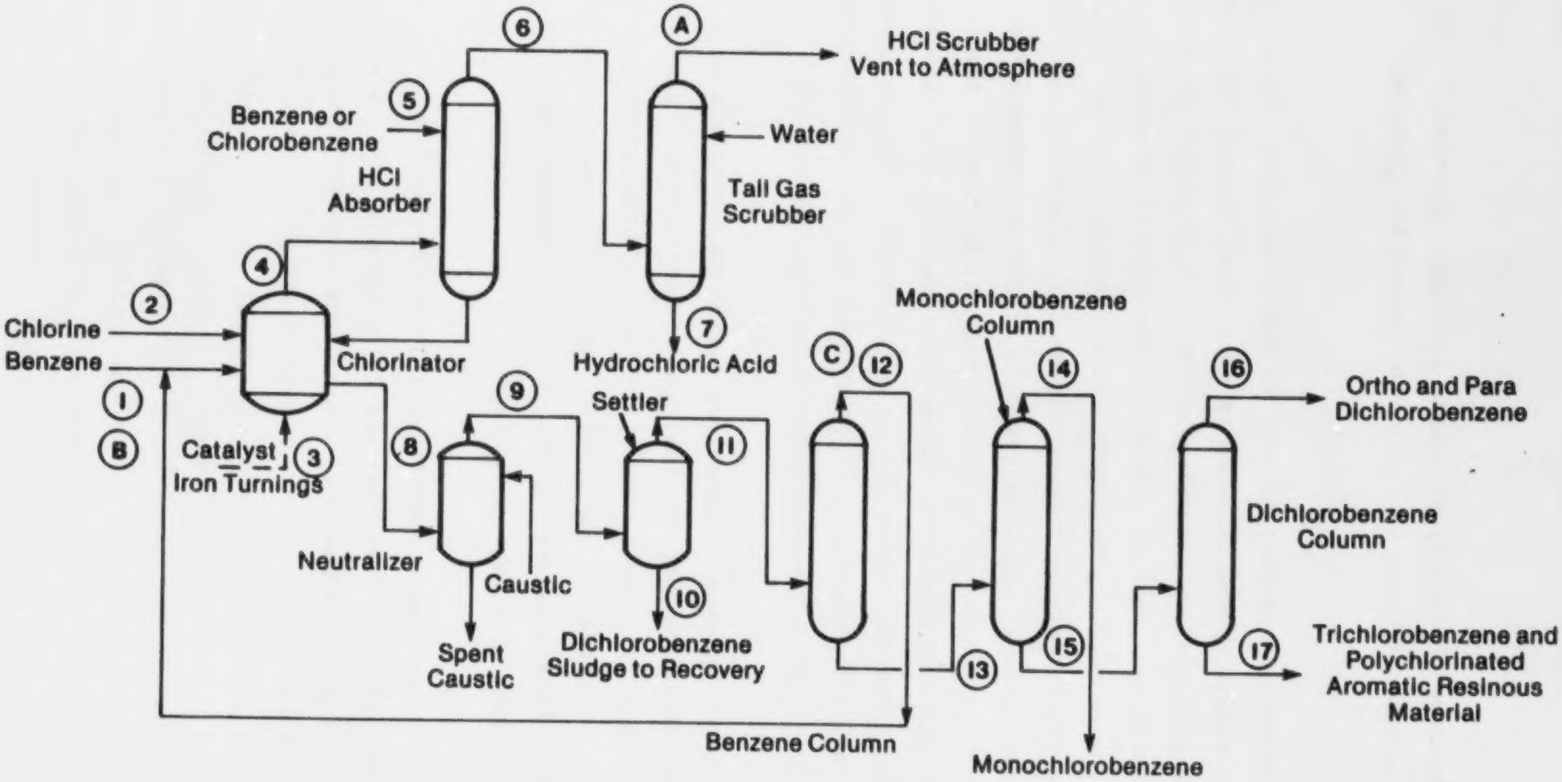
TABLE 23. UNITED STATES PRODUCERS OF MONO-, DI-, AND TRICHLOROBENZENE[11]

Company	Location	Product	Annual Capacity (10^6 lb)
Monsanto Chemical Company	Sauget, IL	Monochlorobenzene	176
		o-Dichlorobenzene	10
		p-Dichlorobenzene	25
PPG Industries, Inc. Chemical Group	Natrium, WV	Monochlorobenzene	45
		o-Dichlorobenzene	20
		p-Dichlorobenzene	30
Standard Chlorine Chemical Company	Delaware City, DE	Monochlorobenzene	150
		o-Dichlorobenzene	50
		p-Dichlorobenzene	75
		1,2,3-Trichlorobenzene	NA[a]
		1,2,4-Trichlorobenzene	NA[a]
Specialty Organics, Inc.	Irwindale, CA	o-Dichlorobenzene	2[b]
		p-Dichlorobenzene	2[b]
Southland Corporation Chemical Division	Great Meadows, NJ	1,3,5-Trichlorobenzene	NA[a]

[a] NA = not available.

[b] This facility is a processor and purchases mixtures of chlorobenzene to isolate o- and p-dichlorobenzene.

Note: These are lists of major facilities producing mono-, di-, and trichlorobenzene. These lists are subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of emissions from any given facility is a function of variables, such as throughput and control measures, and should be determined through direct contacts with plant personnel. These data on producers and locations are as of January 1987.


HCl Scrubber
Vent to Atmosphere
A
6
5
Benzene or
Chlorobenzene
HCl
Absorber
Water
Tail Gas
Scrubber
4
2
Chlorine
Benzene
1
B
Chlorinator
Catalyst
Iron Turnings
3
7
Hydrochloric Acid
C
12
Monochlorobenzene
Column
14
16
Ortho and Para
Dichlorobenzene
9
Settler
8
11
Neutralizer
Caustic
10
Spent
Caustic
Dichlorobenzene
Sludge to Recovery
Dichlorobenzene
Column
13
15
17
Trichlorobenzene and
Polychlorinated
Aromatic Resinous
Material
Benzene Column
Monochlorobenzene
3870077R

Note: Stream numbers correspond to the discussion in the text for this process.
Letters correspond to potential sources of benzene emissions.

Figure 21. Monochlorobenzene and Dichlorobenzene by the Direct Chlorination of Benzene[18, 19, 20]

benzene or chlorobenzene (Stream 5) to remove entrained organics.[20] The HCl is then absorbed in water (Stream 6) to produce commercial grade HCl (Stream 7).

The main chlorobenzene product is sent to the neutralizer (Stream 8), where a 10 percent sodium hydroxide solution is flushed through the crude chlorobenzene to neutralize any remaining acidity. The product is then sent to the settler (Stream 9). Much of the dichlorobenzene is retained in the sludge which is sent to recovery by distillation (Stream 10). The liquid portion is sent to fractionation columns (Stream 11). The first step is to remove the unreacted benzene, which is recycled to the dry benzene feed tank (Stream 12). Monochlorobenzene is separated from the bottoms of the benzene column (Stream 13) and transferred to storage (Stream 14). The remaining product is then fractionated (Stream 15) by distillation. The separated products are run to dichlorobenzene storage (Stream 16) and trichlorobenzene and polychlorinated aromatic resinous material storage (Stream 17).

The primary source of benzene emissions during chlorobenzene production is the tail gas treatment vent of the tail gas scrubber (A in Figure 21). Usually, this vent does not have a control device.[10] Other potential sources of benzene emissions are atmospheric distillation vents from benzene drying column and benzene recovery columns (B and C), process fugitive emissions, and emissions from benzene storage.[10]

Table 24 presents estimated controlled and uncontrolled emission factors for benzene emissions from the tail gas treatment vent, atmospheric distillation vents, fugitive emissions, and benzene storage. The point source factors are based on emissions reported to EPA in response to information requests and trip reports.[10] The fugitive emission factors are based on factors for petroleum refineries.[10] Storage emission factors are based on AP-42 factors for storage tanks.[10] The Appendix provides more detailed descriptions of the derivation of the fugitive and storage emission factors. As noted in Table 24, carbon adsorption is an appropriate control technology for control of emissions from tail gas treatment and distillation

TABLE 24. BENZENE EMISSIONS FROM A HYPOTHETICAL PLANT MANUFACTURING CHLOROBENZENE PRODUCTS[10]

Emission Source	Stream Designation[a]	Uncontrolled Emission Factor g/kg[b]	Control Device or Technique	Emission Reduction (%)	Controlled Emission Factor g/kg[b]
Tail gas treatment	A	0.52	Carbon adsorption	98.7	0.0067
Atmospheric distillation vents	B, C	0.32	Carbon adsorption	98.7	0.0042
Fugitive	---	0.58	Detection and repair of major leaks	71	0.16
Benzene storage	---	0.41	Internal floating roof	85	0.06

[a] Stream designations refer to Figure 21.

[b] Factors are expressed as grams of benzene emitted per kg chlorobenzene product produced. These factors are based on a hypothetical plant producing 68 Gg monochlorobenzene, 12.4 Gg o-dichlorobenzene, and 15.6 Gg p-dichlorobenzene. The reader is urged to contact a specific plant as to process, products made, and control techniques used before applying these emission factors.

column vents. The control technique applicable to process fugitive emissions is an inspection/maintenance program for pumps, valves, and flanges. Internal floating roof tanks may be used to control benzene emissions resulting from benzene storage.[10]

LINEAR ALKYLBENZENE AND BRANCHED ALKYLBENZENE PRODUCTION

Approximately 2.5 percent of benzene production in the United States is used in the production of linear alkylbenzene (LAB). Linear alkylbenzene, or linear alkylate, improves the surfactant performance of detergents. The current demand (including exports) is 565 million pounds (256 million kg); projected 1990 demand is 635 million pounds (288 million kg). Thus, there is a 3 percent projected annual growth rate. The locations of the linear alkylbenzene producers in the United States are shown in Table 25.

Monsanto's Carson plant, Vista's Baltimore plant, and Union Carbide's Institute plant use a monochloroparaffin LAB production process; however, Union Carbide is currently not in operation. Vista's Lake Charles division and Monsanto's Chocolate Bayou division use an olefin process, wherein hydrogen fluoride serves as a catalyst.

The paraffin chlorination process accounts for about 64 percent of the LAB production in the United States. Approximately 36 percent of linear alkylbenzene is produced by the olefin process.

Production of LAB Using the Chlorination Process

The linear alkylbenzene chlorination process takes place with two reactions. In the first step, n-paraffins are chlorinated to monochlorinated n-paraffins. In the second reaction, benzene and crude chloroparaffin is blended with an aluminum chloride catalyst forming crude linear alkylbenzene. The following discussion of LAB production using the chlorination process is taken from Reference 13.

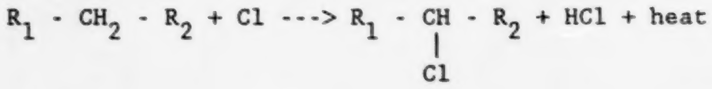
TABLE 25. UNITED STATES PRODUCERS OF ALKYLBENZENE (DETERGENT ALKYLATES)[11]

Company	Location	Annual Capacity (10^6 lb)	Process
Branched Alkylbenzene			
Monsanto Company Monsanto Chemical Company	Carson, CA	NA[a]	---
Linear Alkylbenzene			
Monsanto Company Monsanto Chemical Company	Carson, CA	50	Monochloroparaffin
	Chocolate Bayou, TX	250	Internal olefins, merchant
Vista Chemical Company	Baltimore, MD	225	Internal olefins, merchant and captive
	Lake Charles, LA	150	
TOTAL		675	

[a] Not available.

Note: This is a list of major facilities producing linear and branched alkylbenzene. This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of emissions from any given facility is a function of variables, such as throughput and control measures, and should be determined through direct contacts with plant personnel. These data for producers and locations are as of January 1987.

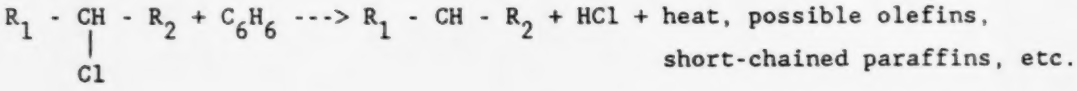
First, n-paraffins are transferred to the n-paraffin feed tank (Stream 1) (Figure 22). The n-paraffins are dried (Stream 2) and routed to the n-paraffin feed tank (Stream 3). The paraffins (in excess) are then sent to the UV catalyzed chlorination reactors (Stream 4) where they are blended with liquid chlorine (Stream 5). The reaction forms n-chloroparaffins (Stream 6) and HCl:



$$R_1 - CH_2 - R_2 + Cl \dashrightarrow R_1 - \underset{\substack{|\\ Cl}}{CH} - R_2 + HCl + \text{heat}$$

Benzene is moved from the bulk storage tank to the feed tank (Stream 7) and is then dried in the benzene azeotropic column (Stream 8). Some benzene emissions can escape from the vent in the column (A_2). The quantity is dependent on the dryness of the benzene and design of the column condenser. The dried benzene is then transferred to the dry benzene feed tank (Stream 9).

The crude chloroparaffin (Stream 10) and an excess of dry benzene (Stream 11) are mixed in an alkylation reactor with an aluminum chloride catalyst. The subsequent reaction produces linear alkylbenzene, illustrated below:



$$R_1 - \underset{\substack{|\\ Cl}}{CH} - R_2 + C_6H_6 \dashrightarrow R_1 - CH - R_2 + HCl + \text{heat, possible olefins, short-chained paraffins, etc.}$$

The HCl gas and some fugitive volatile organics are treated in a VOC absorber (Stream 12) and then an acid absorber (Stream 13). Most of the product goes to hydrochloric acid storage (Stream 14), but some is vented off (A_3). The amount of benzene emissions given off here is dependent on the fluid temperature in the absorber and the vapor pressure of the mixed absorber fluid.

The main product from alkylation are transferred to the catalyst slurry settling tank (Stream 15) to separate crude LAB and catalyst sludge. The sludge is hydrolyzed (Stream 16) to separate the aluminum chloride from

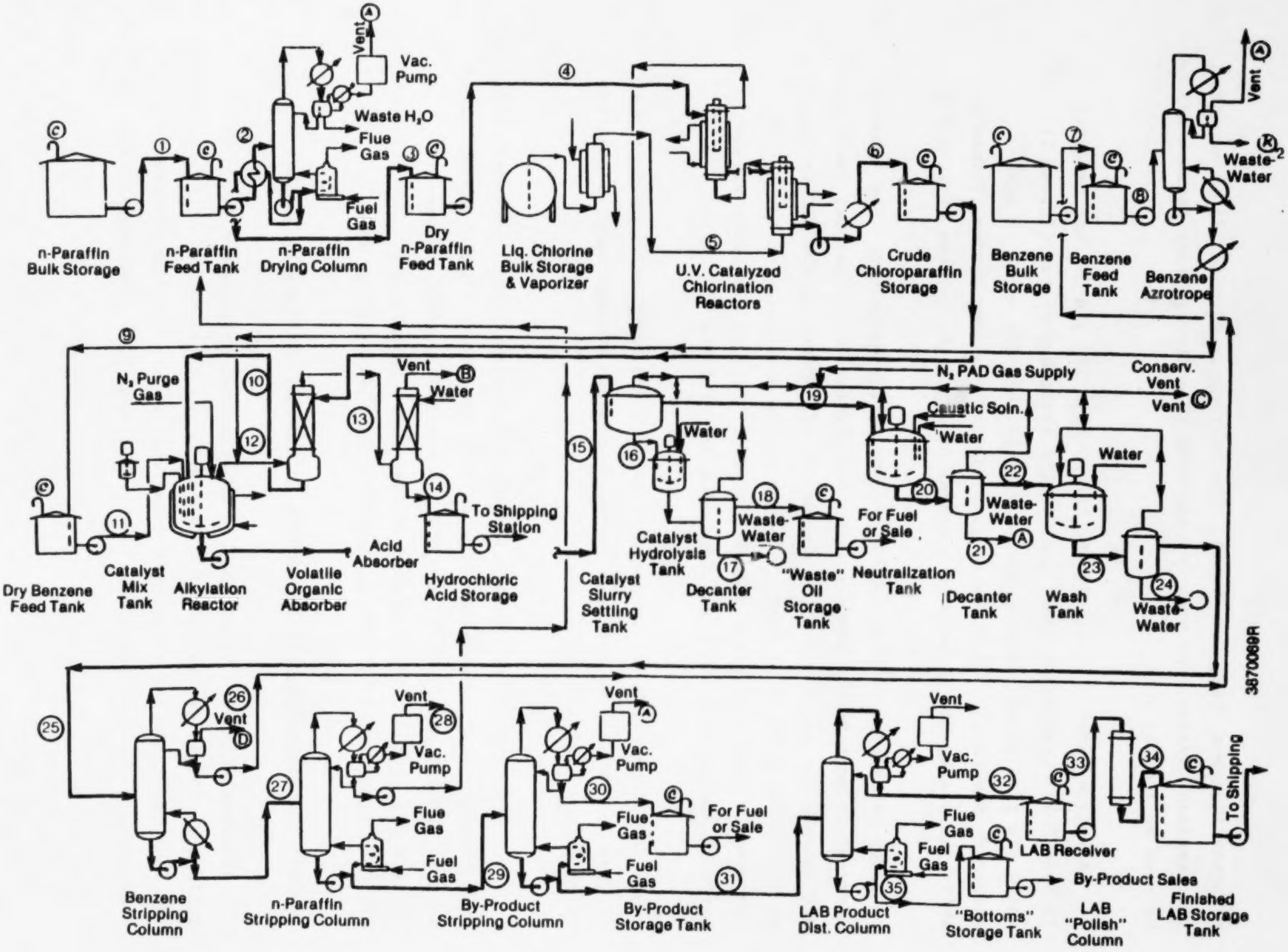

n-Paraffin Bulk Storage
n-Paraffin Feed Tank
n-Paraffin Drying Column
Vac. Pump
Vent
Waste H$_2$O
Flue Gas
Fuel Gas
Dry n-Paraffin Feed Tank
Liq. Chlorine Bulk Storage & Vaporizer
U.V. Catalyzed Chlorination Reactors
Crude Chloroparaffin Storage
Benzene Bulk Storage
Benzene Feed Tank
Benzene Azrotrope
Waste-Water
N$_2$ Purge Gas
Dry Benzene Feed Tank
Catalyst Mix Tank
Alkylation Reactor
Volatile Organic Absorber
Acid Absorber
Water
To Shipping Station
Hydrochloric Acid Storage
Catalyst Slurry Settling Tank
Catalyst Hydrolysis Tank
Decanter Tank
"Waste" Oil Storage Tank
For Fuel or Sale
Neutralization Tank
Caustic Soln.
Decanter Tank
Wash Tank
N$_2$ PAD Gas Supply
Conserv. Vent
Benzene Stripping Column
n-Paraffin Stripping Column
By-Product Stripping Column
By-Product Storage Tank
LAB Product Dist. Column
"Bottoms" Storage Tank
LAB Receiver
By-Product Sales
LAB "Polish" Column
Finished LAB Storage Tank
To Shipping
3870069R

Figure 22. Flow Diagram for LAB Chlorination Process Model Plant with Uncontrolled Emissions[13]

organics (benzene, LAB, tar, etc.). The wastewater (Stream 17) is sent to the treatment system; the organics are sent to a storage tank (Stream 18) to be used as fuel or sold.

Alkaline water neutralizes the LAB (Stream 19) and is then decanted (Stream 20). Wastewater again goes to the treatment system (Stream 21), while the product undergoes a second wash (Stream 22) which is again decanted (Stream 23). Wastewater goes to the treatment system (Stream 24), while the washed LAB is sent to a series of stripping columns (Stream 25).

The benzene is removed by the benzene stripping column. The removed material is sent to the benzene feed tank (Stream 26). Residual inert gases and benzene can be vented (A_5); the amount of benzene in the stream depends on the quantity of inert gases and temperature and design of the reflux condenser. n-Paraffins are then stripped off (Stream 27) under vacuum pressure and sent to the n-paraffin feed tank (Stream 28).

Alkylbenzene and the by-products are removed under vacuum conditions (Stream 29) and are transferred to the by-product storage tank (Stream 30) to be either used as fuel or sold.

The LAB distillation column (Stream 31) separates the "overhead" LAB from the "bottoms" or residual high-boiling materials. The overhead LAB is sent to the LAB receiver (Stream 32), to the LAB "polish" column (Stream 33), then to the finished storage tanks (Stream 34). The "bottoms" are then transferred to storage tanks (Stream 35) prior to sale.

Benzene Emissions from LAB Production Using the Chlorination Process

Benzene emissions using the LAB chlorination process are shown in Table 26. The source designation listed in the table refers to Figure 22. The four major sources of benzene emissions are the benzene azeotropic column vent, the hydrochloric acid absorber vent, the atmospheric wash

TABLE 26. BENZENE EMISSIONS FOR A 90 Gg/Yr HYPOTHETICAL LAB PLANT USING THE CHLORINATION PROCESS[13]

Emission Source[a]	Source Designation[b]	Uncontrolled Emission Factor g/Mg[c]	Control	Controlled Emission Factor g/Mg[c]	Emission Reduction (%)
Benzene Azeotropic Column Vent	A	3.7	Used as fuel	0.00074	99.98
Hydrochloric Acid Absorber Vent	B	250	Used as fuel	0.05	99.98
Atmospheric Wash Decanter Vent	C	12.3	Used as fuel	0.0025	99.98
Benzene Stripping Column Vent	D	3.7	Used as fuel	0.00074	99.98

---

[a] Any given LAB olefin producing plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

[b] Letters refer to vents designated in Figure 22.

[c] Emission factors in terms of g/Mg refer to gram of benzene emitted per megagram of LAB produced by the chlorination process.

decanter vents, and the benzene stripping column vent. The most frequently applied control option for all these sources is to use the emissions for fuel.

Production of LAB Using the Olefin Process

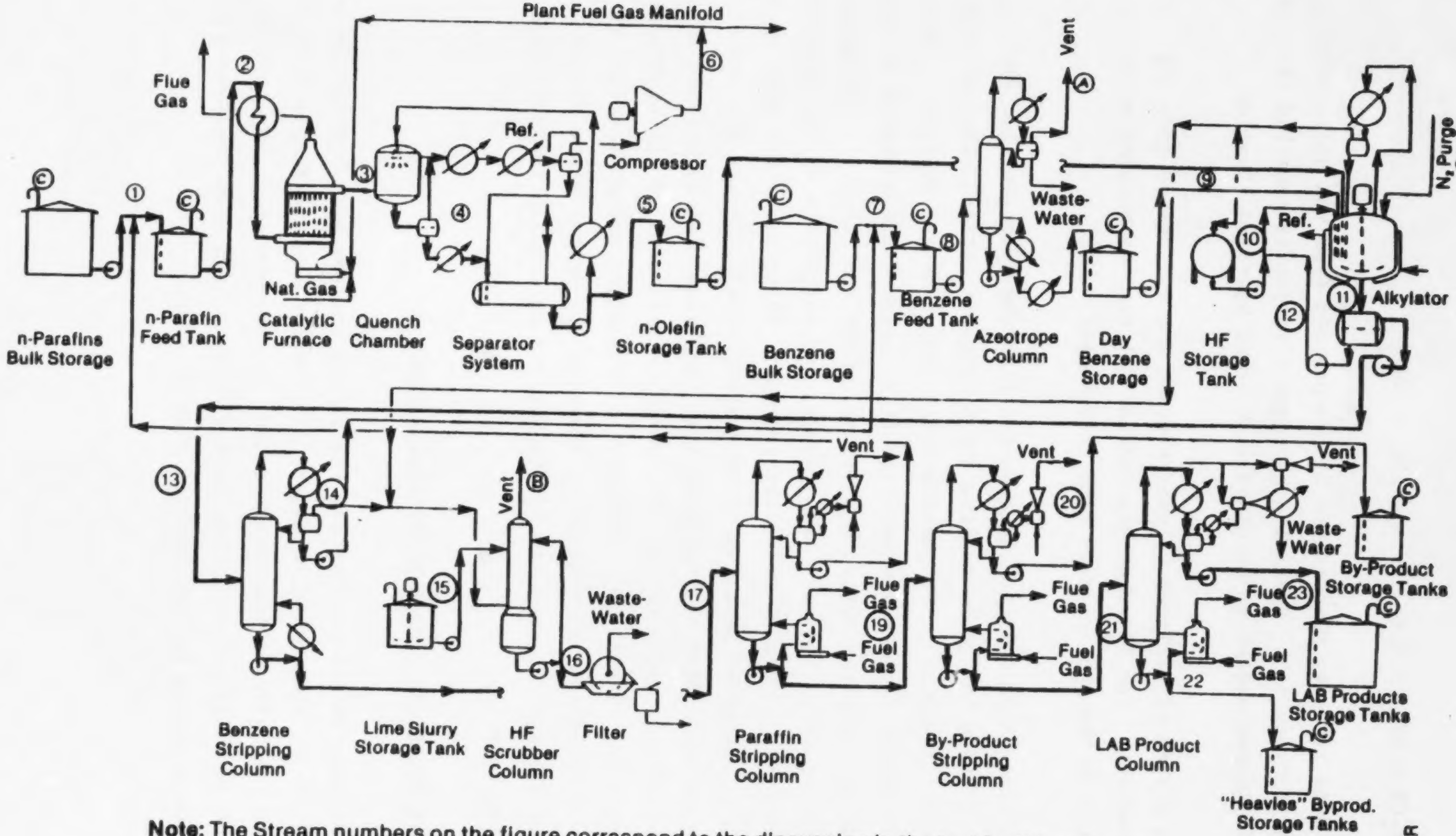
Production of LAB using the olefin process consists of two steps: a dehydrogenation reaction and an alkylation reaction. The n-paraffins are dehydrogenated to n-olefins which are reacted with benzene under the influence of a hydrogen fluoride catalyst to form linear alkylbenzene. The discussion of LAB production using the olefin process is taken from Reference 13.

First, n-paraffins are transferred from bulk storage to the n-paraffin feed tank in Stream 1 (Figure 23). The paraffins are heated to the point of vaporization and passed through a catalyst bed to form n-olefins (Stream 2) by the following reaction:

$$R_1 - CH_2 - CH_2 - R_2 \dashrightarrow R_1\ CH = CH - R_2 + H_2$$

The resulting olefins contain from 10-30 percent alpha olefins, and a mixture of internal olefins, unreacted paraffins, some diolefins, and lower molecular weight "cracked materials." The gas mixture is quickly quenched with a cold liquid stream as it exits to process thermally-promoted side reactions (Stream 3). The gases (e.g., hydrogen, methane, ethane, etc.) are then separated from the olefins (Stream 4), which are stored (Stream 5) while the gas is used as process fuel (Stream 6) or vented to a flare stack.

Benzene is fed from the bulk storage tank to the feed tank (Stream 7) and is dried by azeotropic distillation (Stream 8) to remove all traces of water. An excess of benzene and olefins are transferred and mixed to the alkylation reactor (Stream 9) to be blended with a hydrogen fluoride catalyst (Stream 10). The blend is held at reaction conditions long enough for the alkylation reaction to go to completion as follows:


Plant Fuel Gas Manifold
Flue Gas
Nat. Gas
Ref.
Compressor
Vent
Waste-Water
N₂ Purge Gas
Alkylator
n-Parafins Bulk Storage
n-Parafin Feed Tank
Catalytic Furnace
Quench Chamber
Separator System
n-Olefin Storage Tank
Benzene Bulk Storage
Benzene Feed Tank
Azeotrope Column
Day Benzene Storage
HF Storage Tank
Benzene Stripping Column
Lime Slurry Storage Tank
HF Scrubber Column
Filter
Paraffin Stripping Column
By-Product Stripping Column
LAB Product Column
Fuel Gas
By-Product Storage Tanks
LAB Products Storage Tanks
"Heavies" Byprod. Storage Tanks
① ② ③ ④ ⑤ ⑥ ⑦ ⑧ ⑨ ⑩ ⑪ ⑫ ⑬ ⑭ ⑮ ⑯ ⑰ ⑲ ⑳ ㉑ 22 ㉓
Ⓐ Ⓑ Ⓒ
3870067R

Note: The Stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions (see text).

Figure 23. Flow Diagram for LAB Olefin Process Model Plant[13]

$$R_1CH = CHR_2 + C_6H_6 \text{ ---> } R_1CH_2 - CHR_2$$

The liquid hydrogen fluoride is then separated from the hydrocarbon in the settler (Stream 11). Remaining hydrogen fluoride is recycled (Stream 12) to the alkylation vessel to be mixed with fresh hydrogen fluoride.

A series of stripper columns extract the essentials from the hydrocarbons. The first column (Stream 13) removes benzene which is recycled to the benzene feed tank (Stream 14).

A lime water solution is then fed into the hydrogen fluoride scrubber column (Stream 15) to neutralize the hydrogen fluoride. The solution is filtered (Stream 16); the wastewater is routed to the treatment facility and the solids are transferred to a landfill. Some benzene can be emitted through the hydrogen fluoride scrubber column vent (A_2). Inert gases and air venting from the unit, temperature, and purge rate of the scrubber can influence the amount of volatiles emitted. These gases are usually sent to a flare. Unreacted paraffin is then stripped off (Stream 17) and returned to the paraffin feed tank (Stream 18). Any remaining by-product is removed by the next stripping column (Stream 19) and is sent to the by-product storage tanks (Stream 20). The last distillation column purifies the main linear alkylbenzene (Stream 21). "Heavies" by-products are stored (Stream 22) and the pure LAB is transferred to storage tanks (Stream 23) awaiting sale.

Process Emissions from the LAB Olefin Process

Benzene emissions from the LAB olefin process are shown in Table 27. The two major sources of emissions are the benzene azeotropic column vent (A) and the hydrogen fluoride scrubber column vent (B). The control for both of these emissions is use as fuel. Emissions from the hydrogen fluoride scrubber column vent can also be flared.

TABLE 27. BENZENE EMISSIONS FOR A 90 Gg/Yr HYPOTHETICAL LAB PLANT USING THE OLEFIN PROCESS[13]

Emission Source[a]	Source Designation[b]	Uncontrolled Emission Factor g/Mg[c]	Control	Controlled Emission Factor g/Mg[c]	Emission Reduction (%)
Benzene Azeotropic Column Vent	A	3.7	Used as fuel	0.00074	99.98
Hydrogen Fluoride Scrubber Column Vent	B	11	Used as fuel	0.0022	99.98
			Flare	1.1	90

[a] Any given LAB olefin producing plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

[b] Letters refer to vents designated in Figure 23.

[c] Emission factors in terms of g/Mg refer to gram of benzene emitted per megagram of LAB produced by the olefin process.

MALEIC ANHYDRIDE PRODUCTION

Maleic anhydride is now produced in the United States using n-butane. In the past, a benzene based process had been used.[11] For reference, a brief description of the benzene based maleic anhydride process is provided here.

Process Description

With the benzene process, maleic anhydride was produced by oxidizing benzene in the presence of a catalyst.[10] A mixture of vaporized benzene and air were sent to a fixed bed reactor. The catalyst for the oxidation reaction was vanadium or molybdenum oxide on inert carriers. The stream was then sent to a cooler, a condenser, and a separator, in which the maleic anhydride was condensed and separated. The maleic anhydride was then dehydrated by azeotropic distillation using xylene. The crude product is then aged and sent to a fractionation column that yielded molten maleic anhydride as the product.[10]

Sources of benzene emissions from the benzene oxidation process included main process vents, refining vacuum vents, fugitive emissions, and emissions from waste handling and disposal.[10]

Again, maleic anhydride is now produced in the United States completely through a n-butane process. This description of the benzene process was provided for reference.

GASOLINE MARKETING

Gasoline storage and distribution activities represent potential sources of benzene emissions. The benzene content of gasoline ranges from less than 1 to almost 2 percent by liquid volume, but typical concentrations are around 1.2 percent by volume.[14] Therefore, total hydrocarbon emissions resulting from storage tanks, material transfer, and vehicle fueling include emissions of benzene. This section describes sources of benzene emissions from gasoline marketing operations. Because the sources of these emissions are so widespread, individual locations are not identified in this section. Instead, emission factors are presented, along with a general discussion of the sources of these emissions. The discussion is taken from Reference 21.

The flow of the gasoline marketing system in the United States is shown in Figure 24. From the refinery, gasoline may be transported by pipeline, rail, ship, or barge to intermediate stations known as bulk terminals. Terminals are bulk wholesale marketing outlets, of which there are about 1,500 nationwide.[22] From the bulk terminal, tank trucks deliver gasoline to the national network of about 15,000 bulk plants.[22] Daily throughput at a terminal averages about 950,000 liters (250,000 gallons) and is greater than the average 19,000 liters (5,000 gallons) daily throughput of a bulk plant.[22] Both bulk terminals and bulk plants deliver gasoline to private, commercial, and retail customers.

The transport of gasoline with marine vessels, distribution at bulk plants, and distribution at service stations and associated benzene emissions are discussed below.

Benzene Emissions from Loading Marine Vessels

Volatile organic compounds (VOC) can be emitted as crude oil and refinery products (gasoline, distillate oil, etc.) and are loaded and transported by marine tankers and barges. Loading losses are the primary source of evaporative emissions from marine vessel operations.[23] These emissions occur as vapors in "empty" cargo tanks are expelled into the atmosphere as liquid is added to the cargo tank. The vapors may be composed of residual material left in the "empty" cargo tank and/or the material being added to the tank. Therefore, the exact composition of the vapors emitted during the loading process are difficult to determine.

Emission factors for volatile organic compounds from marine vessel loading were found in EPA documents.[23] Assuming a benzene/VOC ratio of 0.006 (Reference 21), emission factors for benzene from marine vessel loading are given in Table 28. Factors are available for crude oil,

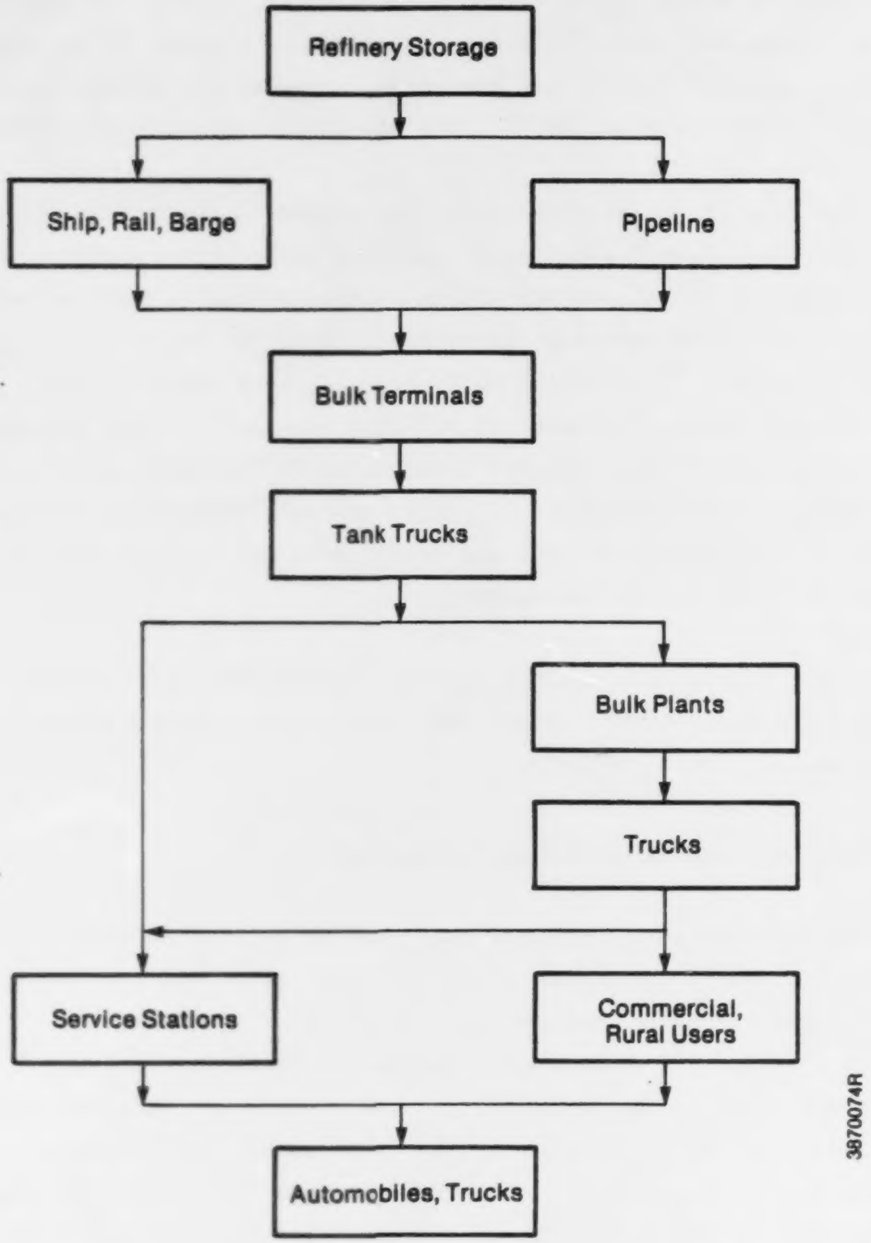

Refinery Storage
Ship, Rail, Barge
Pipeline
Bulk Terminals
Tank Trucks
Bulk Plants
Trucks
Service Stations
Commercial, Rural Users
Automobiles, Trucks
3870074R

Figure 24. The Gasoline Marketing Distribution System in the United States[21]

TABLE 28. UNCONTROLLED VOLATILE ORGANIC COMPOUND AND BENZENE EMISSIONS FROM LOADING GASOLINE IN MARINE VESSELS[21,23]

Emission Source	Volatile Organic Compound Emission Factor (mg/l Transferred)	Benzene Emission Factor (mg/l Transferred)
Tanker Ballasting	100	0.6
Transit	320[c]	1.9[c]
Ship/Ocean Barge:[d]		
Uncleaned; volatile previous cargo	315	1.9
Ballasted; volatile previous cargo	205	1.2
Cleaned; volatile previous cargo	180	1.1
Gas-freed; volatile previous cargo	85	0.5
Any condition; nonvolatile previous cargo	85	0.5
Typical situation; any cargo	215	1.3
Barge:		
Uncleaned; volatile previous cargo	465	2.8
Gas-freed; any cargo	245	1.5
Typical situation; any cargo	410	2.5

[a] Factors are for nonmethane-nonethane VOC emissions.

[b] Based on benzene/VOC ratio of 0.006 (Reference 21).

[c] Units for this factor are mg/week-liter transported.

[d] Ocean barge is a vessel with compartment depth of 40 feet; barge is a vessel with compartment depth of 10-12 feet.

distillate oil, and other fuels.[23] However, reliable estimates of the benzene content of these fuels were not found. Therefore, it was not possible to provide benzene emission factors for marine vessel loading of fuels other than gasoline.

Benzene Emissions from Bulk Gasoline Plants, Bulk Gasoline Terminals and Service Stations

Each operation in which gasoline is transferred or stored is a potential source of benzene emissions. At bulk terminals and bulk plants, loading and unloading gasoline and storing gasoline are sources of benzene emissions. The gasoline that is stored in above ground tanks is pumped through loading racks that measure the amount of product. The loading racks consist of pumps, meters, and piping to transfer the gasoline or other liquid petroleum products. Loading of gasoline into tank trucks can be accomplished by one of three methods: splash, top submerged, or bottom loading. In splash loading, gasoline is introduced into the tank truck directly through a compartment located on the top of the truck.[21] Top submerged loading is done by attaching a downspout to the fill pipe so that gasoline is added to the tank truck near the bottom of the tank. Bottom loading is the loading of product into the truck tank from the bottom. Because emissions occur when the product being loaded displaces vapors in the tank being filled, top submerged loading and bottom loading reduce the amount of material (including benzene) that is emitted.[21]

Vapor balancing systems, consisting of a pipeline between the vapor spaces of the truck and the storage tanks, are closed systems. These systems allow the transfer of vapor displaced by liquid in the storage tank into the transfer truck as gasoline is put into the storage tank.[21] Table 29 lists emission factors for gasoline vapor and benzene from gasoline loading racks at bulk terminals and bulk plants. The gasoline vapor emission factors were taken from AP-42 (Reference 23). The benzene factors were obtained by multiplying the gasoline vapor factor by the average benzene content of the vapor (0.006 percent).[21]

TABLE 29. BENZENE EMISSION FACTORS FOR GASOLINE LOADING AND BULK TERMINALS AND BULK PLANTS[21]

Loading Method	Gasoline Vapor Emission Factor[a] mg/l	Benzene Emission Factor[b] mg/l
Splash	1430	8.6
Submerged[c]	590	3.5
Balance Service	980	5.9

[a] From AP-42 (Reference 23). Gasoline factors represent emissions of nonmethane-nonethane VOC. Factors are expressed as mg gasoline vapor per mg gasoline transferred.

[b] Based on a benzene/VOC ratio of 0.006 (Reference 21).

[c] Submerged loading is either top or bottom submerged.

A more recent study has provided another estimate of the benzene content of gasoline vapors.[22] An EPA test program was designed to characterize refueling emissions. Results of the study showed 0.0079 g benzene/g hydrocarbon in the refueling emissions. The author of the EPA report summarizing the test results indicated that an estimate of 0.0079 g benzene/g hydrocarbon was quite similar to the 0.006 g/g hydrocarbon estimate developed earlier. The difference in the two estimates is likely attributed to differences in the benzene content of gasoline and the fact that the original reference (Reference 21) did not take dynamic effects such as liquid/vapor turbulence into account.[22]

Storage emissions of benzene at bulk terminals and bulk plants depend on the type of storage tank used. A typical bulk terminal may have four or five above ground storage tanks with capacities ranging from 1,500-15,000 m^3.[21] Most tanks in gasoline service have an external floating roof to prevent the loss of product through evaporation and working losses. Fixed-roof tanks, still used in some areas to store gasoline, use pressure-vacuum vents to control breathing losses. Some tanks may use vapor balancing or processing equipment to control working losses. A breather valve (pressure-vacuum valve), which is commonly installed on many fixed-roof tanks, allows the tank to operate at a slight internal pressure or vacuum.

The major types of emissions from fixed-roof tanks are breathing and working losses. Breathing loss is the expulsion of vapor from a tank vapor space that has expanded or contracted because of daily changes in temperature and barometric pressure. The emissions occur in the absence of any liquid level change in the tank. Combined filling and emptying losses are called "working losses." Emptying losses occur when the air that is drawn into the tank during liquid removal saturates with hydrocarbon vapor and expands, thus exceeding the fixed capacity of the vapor space and overflowing through the pressure vacuum valve.

A typical external floating-roof tank consists of a cylindrical steel shell equipped with a deck or roof that floats on the surface of the stored liquid, rising and falling with the liquid level. The liquid surface is completely covered by the floating roof except in the small annular space between the roof and the shell. A seal attached to the roof touches the tank wall (except for small gaps in some cases) and covers the remaining area. The seal slides against the tank wall as the roof is raised or lowered. The floating roof and the seal system serve to reduce the evaporative loss of the stored liquid.

An internal floating-roof tank has both a permanently affixed roof and a roof that floats inside the tank on the liquid surface (contact roof), or supported on pontoons several inches above the liquid surface (noncontact roof). The internal floating-roof rises and falls with the liquid level, and helps to restrict the evaporation of organic liquids.

Losses from floating-roof tanks include standing-storage losses and withdrawal losses. Standing-storage losses, which result from causes other than a change in the liquid level, constitute the major source of emissions from external floating-roof tanks. The largest potential source of these losses is an improper fit between the seal and the tank shell (seal losses). As a result, some liquid surface is exposed to the atmosphere. Air flowing over the tank creates pressure differentials around the floating roof. Air flows into the annular vapor space on the leeward side and an air-vapor mixture flows out on the windward side.

Withdrawal loss is another source of emissions from floating-roof tanks. When liquid is withdrawn from a tank, the floating roof is lowered and a wet portion of the tank wall is exposed. Withdrawal loss is the vaporization of liquid from the wet tank wall.

Table 30 shows emission factors for storage tanks at a typical bulk terminal. The emission factors were based on AP-42 factors and the weight fraction of benzene in the vapor of 0.006.[21]

The two basic types of gasoline loading into tank trucks at bulk plants are the same as those used at terminals. The first is the splash filling method, which usually results in high levels of vapor generation and loss.

TABLE 30. BENZENE EMISSION FACTORS FOR STORAGE LOSSES AT A TYPICAL GASOLINE BULK TERMINAL[21]

Storage Method	Benzene Emission Factor Mg/yr/Tank[a]
Fixed Roof[b]	
Working Loss	0.2
Breathing Loss	0.05
External Floating Roof[c]	
Working Loss	d
Storage Loss	
- Primary Seal	0.05
- Secondary Metallic Shoe Seal	0.02

[a] Terminal with 950,000 liters/day (250,000 gallons/day) with four storage tanks for gasoline. See Appendix A for derivation.

[b] Typical fixed-roof tank based upon capacity of 2,680 m^3 (16,750 bbls.).

[c] Typical floating-roof tank based upon capacity of 5,760 m^3 (36,000 bbls.).

[d] Emission factor = $(0.46 \times 10^{-7}\ Q)$ Mg/yr, where Q is the throughput through the tanks in barrels (Reference 21).

The second method is submerged filling with either a submerged fill pipe or bottom filling, which significantly reduces liquid turbulence and vapor-liquid contact resulting in much lower emissions. Table 31 shows the uncontrolled emission factors for benzene from a typical bulk plant.

Gasoline tank trucks have been demonstrated to be major sources of vapor leakage. Some vapors may leak uncontrolled to the atmosphere from dome cover assemblies, pressure-vacuum (P-V) vents, and vapor collection piping and vents. Other sources of vapor leakage on tank trucks that occur less frequently include tank shell flaws, liquid and vapor transfer hoses, improperly installed or loosened overfill protection sensors, and vapor couplers. Since terminal controls are usually found in areas where trucks are required to collect vapors after delivery of product to bulk plants or service stations (balance service), the gasoline vapor emission factor associated with uncontrolled truck leakage was assumed to be 30 percent of the balance service truck loading factor (960 mg/liter x 0.30 = 288 mg/liter).[21] Thus the emission factor for benzene emissions from uncontrolled truck leakage is 1.7 mg/liter, based on a benzene/vapor ratio of 0.006.

The discussion on service station operations is divided into two areas: the filling of the underground storage tank and automobile refueling. Although terminals and bulk plants also have two distinct operations (tank filling and truck loading), the filling of the underground tank at the service station ends the wholesale gasoline marketing chain. The automobile refueling operations interact directly with the public and control of these operations can be performed by putting control equipment on either the service station or the automobile.

Benzene Emissions from Service Stations--

Normally, gasoline is delivered to service stations in large tank trucks from bulk terminals or smaller account trucks from bulk plants. Emissions are generated when hydrocarbon vapors in the underground storage

TABLE 31. UNCONTROLLED GASOLINE VAPOR AND BENZENE EMISSIONS FROM A TYPICAL BULK PLANT[21]

Emission Source[a]	Gasoline Vapor Emission Factor mg/liter	Benzene Emission Factor[b] mg/liter
Storage Tanks - Fixed Roof		
Breathing Loss	600	3.6
Filling Loss	1150	6.9
Draining Loss	460	2.7
Gasoline Loading Racks		
Splash Loading	1430	8.6
Submerged Loading	590	3.5
Submerged Loading (Balance Service)	980	5.9

[a] Typical bulk plant with a gasoline throughput of 19,000 liters/day (5,000 gallons/day).

[b] Based on gasoline emission factor and benzene/vapor ratio of 0.006 (Reference 21).

tank are displaced to the atmosphere by the gasoline being loaded into the tank. As with other loading losses, the quantity of the service station tank loading loss depends on several variables, including the quantity of liquid transferred, size and length of the fill pipe, the method of filling, the tank configuration and gasoline temperature, vapor pressure, and composition. A second source of emissions from service station tankage is underground tank breathing. Breathing losses occur daily and are attributed to temperature changes, barometric pressure changes, and gasoline evaporation.

In addition to service station tank loading losses, vehicle refueling operations are considered to be a major source of emissions. Vehicle refueling emissions are attributable to vapor displaced from the automobile tank by dispensed gasoline and to spillage. The major factors affecting the quantity of emissions are gasoline temperature, auto tank temperature, gasoline Reid vapor pressure (RVP), and dispensing rates. Table 32 lists the uncontrolled emissions from a typical gasoline service station. The emission factors presented in Table 32 are from EPA's AP-42 document (Reference 23).

Control Technology for Gasoline Transfer

At bulk terminals and bulk plants, benzene emissions from gasoline transfer may be controlled by a vapor processing system in conjunction with a vapor collection system.[21] Figure 25 shows a Stage I control vapor balance system at a bulk plant. These systems collect and recover gasoline vapors from empty, returning tank trucks as they are filled with gasoline from storage tanks.[23]

At service stations, vapor balance systems contain the gasoline vapors within the station's underground storage tanks for transfer to empty gasoline tank trucks returning to the bulk terminal or bulk plant. Figure 26 shows a diagram of a service station vapor balance system.

TABLE 32. UNCONTROLLED GASOLINE VAPOR AND BENZENE EMISSIONS FROM A TYPICAL SERVICE STATION[21,24]

Emission Source[a]	Gasoline Vapor Emission Factors mg/liter	Benzene Emission Factors[b] mg/liter
Underground Storage Tanks		
Tank Filling Losses		
- Submerged Fill	880	5.3
- Splash Fill	1380	8.3
- Balanced Submerged Filling	40	0.2
Breathing Losses	120	0.7
Automobile Refueling		
Displacement Losses		
- Uncontrolled	1320	7.9
- Controlled	132	0.8
Spillage	84	0.5

[a] Typical service station has a gasoline throughput of 190,000 liters/month (50,000 gallons/month).

[b] Based on gasoline vapor emission factor and benzene/vapor ratio of 0.006 (Reference 21).

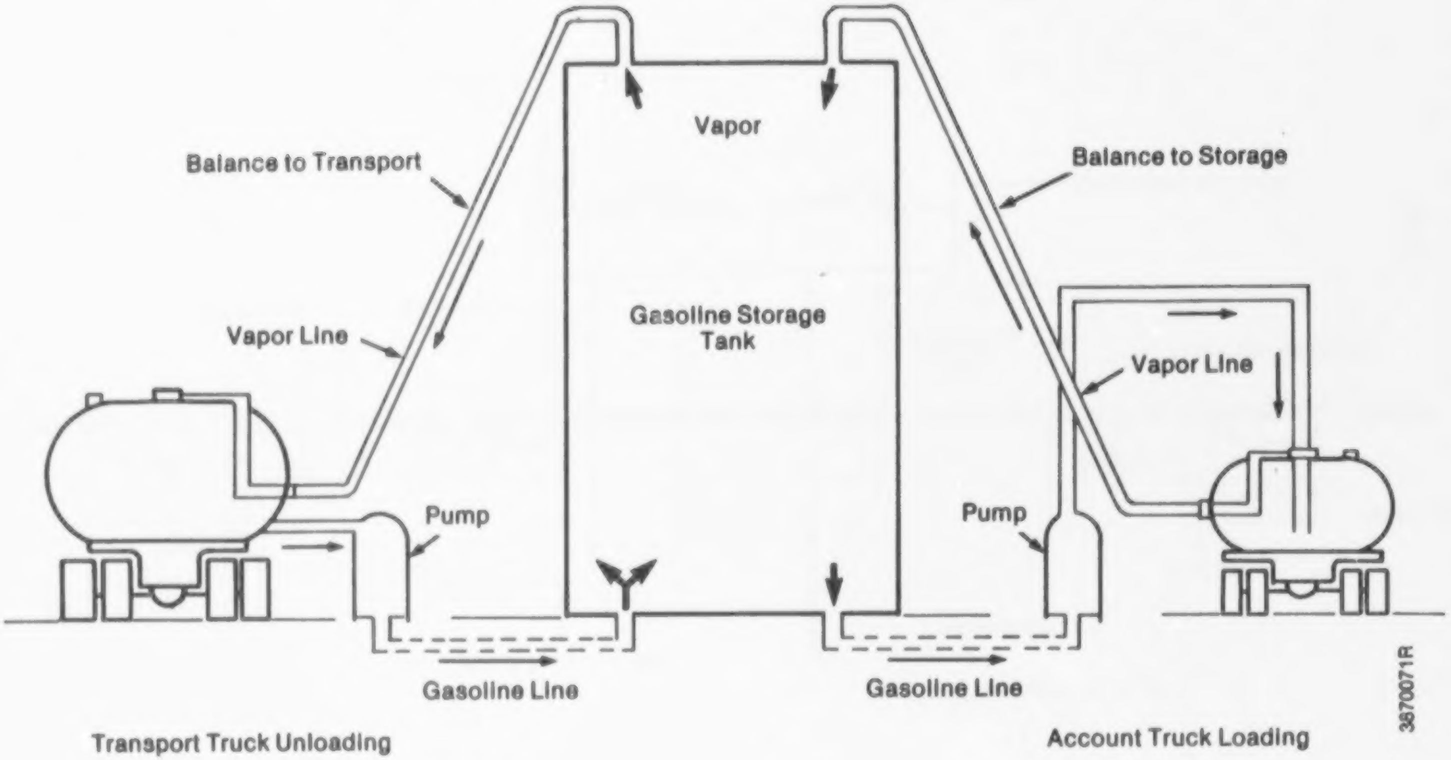

Balance to Transport
Vapor Line
Pump
Gasoline Line
Transport Truck Unloading
Vapor
Gasoline Storage Tank
Balance to Storage
Vapor Line
Pump
Gasoline Line
Account Truck Loading
3870071R

Figure 25. Bulk Plant Vapor Balance System[21]

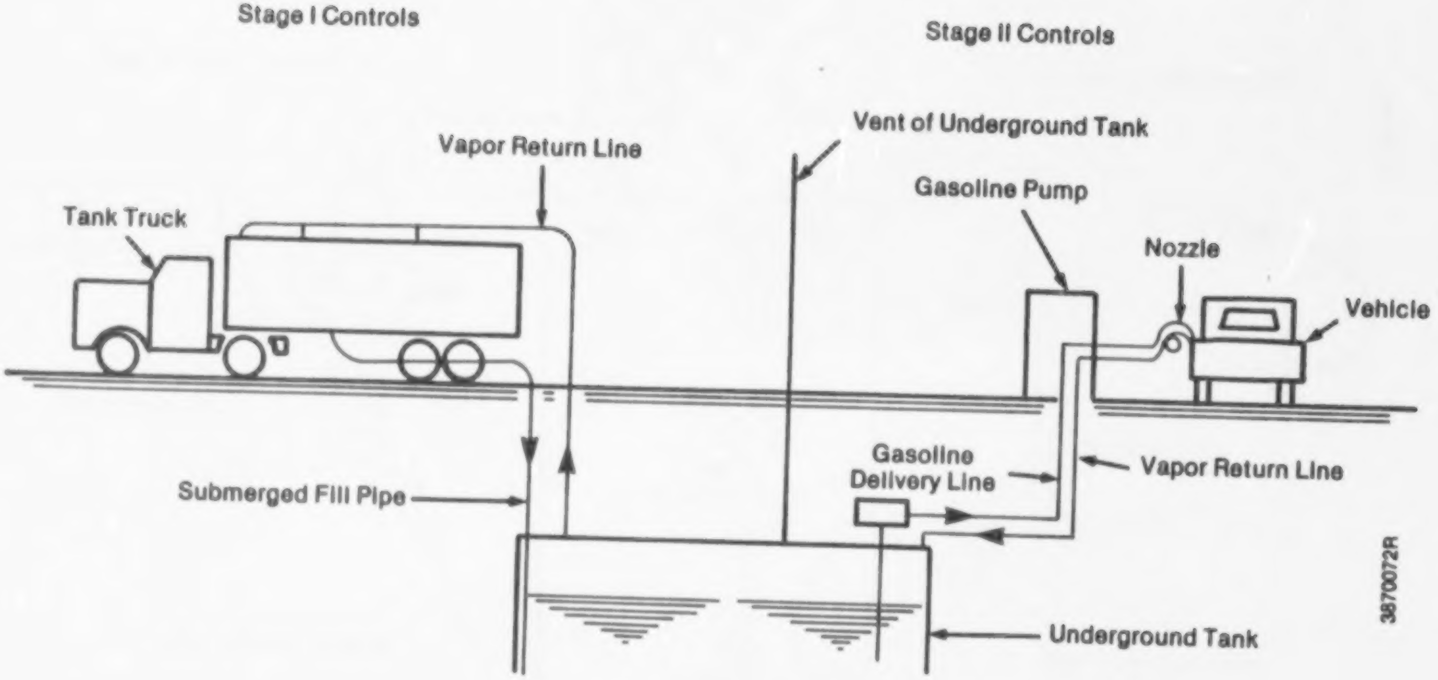

Stage I Controls
Stage II Controls
Vent of Underground Tank
Vapor Return Line
Gasoline Pump
Tank Truck
Nozzle
Vehicle
Gasoline Delivery Line
Vapor Return Line
Submerged Fill Pipe
Underground Tank
3870072R

Figure 26. Service Station Vapor Balance System[21]

Control Technology for Gasoline Storage

The control technologies for controlling benzene emissions from gasoline storage involve upgrading the type of storage tank used or addition of a vapor control system. For fixed-roof tanks, emissions are most readily controlled by installation of internal floating roofs.[21] An internal floating roof reduces the area of exposed liquid surface on the tank and, therefore, decreases evaporative loss. Installing an internal floating roof in a fixed-roof tank can reduce total emissions by 68.5 to 97.8 percent.[21]

For external floating-roof tanks, no control measures have been identified for controlling withdrawal losses and emissions.[21] These emissions are functions of the turnover rate of the tank and the characteristics of the tank shell. Rim seal losses in external floating roof tanks depend on the type of seal. Liquid-mounted seals are more effective than vapor-mounted seals in reducing rim seal losses.[21] Metallic shoe seals are more effective than vapor-mounted seals but less effective than liquid-mounted seals.[21]

Control Technology for Vehicle Refueling Emissions

Vehicle refueling emissions are attributable to vapor displaced from the automobile tank by dispensed gasoline and to spillage. The quantity of displaced vapors is dependent on gasoline temperature, vehicle tank size and temperature, fuel level, gasoline RVP, and dispensing rates.[21]

The two basic refueling vapor control alternatives are: control systems on service station equipment (Stage II controls), and control systems on vehicles (onboard controls). Onboard controls are basically limited to the carbon canister.

There are currently three types of Stage II systems in limited use in the United States: the vapor balance, the hybrid, and the vacuum assist systems. In the vapor balance system, gasoline vapor in the automobile fuel tank is displaced by the incoming liquid gasoline and is prevented from escaping to the atmosphere at the fillneck/nozzle interface by a flexible rubber "boot." This boot is fitted over the standard nozzle and is attached to a hose similar to the liquid hose. The hose is connected to piping which vents to the underground tank. An exchange is made (vapor for liquid) as the liquid displaces vapor to the underground storage tank. The underground storage tank assists this transaction by drawing in a volume of vapor equal to the volume of liquid removed.[21]

The vacuum assist system differs from the balance system in that a "blower" (a vacuum pump) is used to provide an extra pull at the nozzle/fillneck interface. Assist systems can recover vapors effectively without a tight seal at the nozzle/fillpipe interface because only a close fit is necessary. A slight vacuum is maintained at the nozzle/fillneck interface allowing air to be drawn into the system and not allowing the vapors to escape. Because of this assist, the interface "boot" need not be as tight fitting as with balance systems. Further, the vast majority of assist nozzles do not require interlock mechanisms. Assist systems generally have vapor passage valves located in the vapor passage somewhere other than in the nozzles, resulting in a nozzle which is less bulky and cumbersome than nozzles employed by vapor balance systems.[21]

The hybrid system borrows from the concepts of both the balance and vacuum assist systems. It is designed to enhance vapor recovery at the nozzle/fillneck interface by vacuum, while keeping the vacuum low enough so that a minimum level of excess vapor/air is returned to the underground storage tank.

With the hybrid system, a small amount of the liquid gasoline (less than 10 percent) pumped from the storage tank is routed (before metering) to a restricting nozzle called an aspirator. As the gasoline goes through this restricting nozzle, a small vacuum is generated. This vacuum is used to draw vapors into the rubber boot at the interface. Because the vacuum is so small, very little excess air, if any, is drawn into the boot, hose and underground storage tank, and thus there is no need for a secondary processor, such as the vacuum assist's incinerator.[21]

Onboard vapor control systems consist of carbon canisters installed on the vehicle to control refueling emissions. The carbon canister system adsorbs, on activated carbon, the vapors which are displaced from the vehicle fuel tank by the incoming gasoline. Such a system first absorbs the emissions released during refueling and subsequently purges these vapors from the carbon to the engine carburetor when it is operating. This system is essentially an expansion of the present evaporative emissions control system used in all new cars to minimize breathing losses from the fuel tank and to control carburetor evaporative emissions. However, unlike the present system, a refueling vapor recovery system will require a tight seal at the nozzle/fillneck interface during refueling operations to ensure vapors flow into the carbon canister and are not lost to the atmosphere.[21]

BENZENE EMISSIONS FROM MOTOR VEHICLES

Hydrocarbons may be emitted from gasoline-powered vehicles from the carburetor (evaporation), fuel tank (vents), crankcase (blow-by past piston rings), and engine exhaust.[25] The level of benzene emissions from these sources depends on the gasoline blend. If the fuel contains ethylbenzene, for example, incomplete combustion may lead to conversion of ethylbenzene to benzene.[25] Furthermore, there is some evidence that toluene dealkylation occurs, producing small amounts of benzene that are emitted.[26] In an experiment using a fuel mixture containing hydrocarbons and toluene but no benzene, benzene was found in the exhaust of single cylinder engines.[26] According to another author, more than 50 percent of the benzene emitted from motor vehicles is formed during the combustion of gasoline and is not from the benzene present in the fuel.[27] Therefore, more benzene may be found in vehicle exhaust than was originally present in the fuel.[14]

Emissions of benzene from vehicle exhaust vary by vehicle type, fuel type, and control technology in use. Table 33 lists the fractions of vehicle exhaust and evaporative emissions for several different vehicle types. The data in Table 33 were derived from tests on low mileage, well maintained vehicles. Then, total hydrocarbons emission factors from the computer program MOBIL3 were speciated for benzene, based on the percentages in Table 33. The resulting 1985 emission factors for benzene from composites of Federal Test Procedures ranged from 0.128 to 0.135 g/mile. The ranges result from the ranges of benzene content in the evaporative emissions (see Table 33).

Control techniques are available and in use for both evaporative and exhaust emissions of benzene. For example, positive crankcase ventilation (PCV) and evaporative controls reduce evaporative emissions of benzene.[14] PCV systems circulate air through the crankcase to pick up blow-by gases and take them to the intake manifold where they enter the combustion chamber.[14] Fuel evaporative controls were installed on all 1971 vehicles.[14] An absorption/regeneration system, one of the most common evaporative control techniques, virtually eliminates evaporative hydrocarbon emissions including benzene.[14] With such a system, a canister of activated carbon traps vapors. The vapors are ultimately fed back to the combustion chamber.

A recent EPA study considered the difference in benzene emissions in vehicle exhaust for vehicles tested under different roadway conditions (urban expressway and stop/go city driving) and the Federal Test Procedure and with different control technologies. The results of the tests are shown in Appendix A, Table A-2. No significant trends were noted when comparing benzene emissions as percentages of the total hydrocarbon emissions for different control technologies.[27] For vehicles under the crowded urban expressway test, benzene emissions ranged from 31.1 mg/mile (no catalyst/air) to 9.4 mg/mile for a three-way catalyst/air (Table A-2). For the simulated "New York City driving" and a vehicle operated with no catalyst/air, the benzene emissions were 150 mg/mile.[27] For the same test situation and a vehicle operating with an oxidation catalyst/no air, the reported benzene emissions were 170 mg/mile (Table A-2).[27]

TABLE 33. BENZENE EMISSIONS EXPRESSED AS PERCENTAGE OF EXHAUST AND EVAPORATIVE EMISSIONS FOR DIFFERENT VEHICLE CLASSES[28]

Vehicle Class	Benzene Content of Exhaust Hydrocarbons (%)	Benzene Content of Evaporative Hydrocarbons (%)
Light Duty Gasoline Vehicle		0.35 - 1.53[a]
3-way Catalyst	5.12	---
3-way and Oxidation Catalyst	2.78	---
Noncatalyst or Oxidation Catalyst	3.95	---
Light Duty Gasoline Truck	3.24	1.1
Light Duty Diesel Vehicle	2.40	---
Light Duty Diesel Truck	2.40	---
Heavy Duty Gasoline Vehicle	3.48	1.1
Heavy Duty Diesel Vehicle	1.10	---

[a] For fuel-injected vehicles, the range is 0.35 - 0.46 percent. For carbureted light duty gasoline vehicles, the range is 1.11 - 1.53 percent.

BENZENE USE AS A SOLVENT

More than 95 percent of all benzene used as a raw material is used in producing the chemicals [illegible] in this section. However, benzene has also been used in a [illegible] of operations as a solvent. Table 34 lists industries and products in which benzene has reportedly been used as a solvent. However, for a number of reasons including cost and potential adverse health effects, the use of benzene as a solvent has been decreasing. In 1971, about 8 percent of benzene produced was used in solvent applications.[29] In 1982, benzene use as a solvent accounted for only 1 percent of the total amount produced.[29] Of the source categories or products listed in Table 34, ten have reportedly discontinued use of benzene as a solvent.

Telephone contacts with industry sources and trade associations in some of the categories listed in Table 34 shows that benzene use as a solvent was declining or had ceased in those industries. For example, as of 1983, a trade association contact reported that benzene was generally no longer used in textile manufacture. However, benzene has been found in wastewaters from textile finishing and non-woven manufacturing plants.[29] Similar reports of decreased benzene use as a solvent were received from other industry contacts, including representatives of the degreasing source category, pharmaceuticals manufacture, and general organic synthesis.[29,30]

However, benzene is used as a denaturant for ethyl alcohol and as an azeotropic agent for dehydration of 95 percent ethanol and 91 percent isopropanol.[30] Companies producing these alcohols are shown in Table 35. No specific data were found concerning emissions of benzene from these facilities.

Benzene is also used in aluminum alkyls production. Producers of aluminum alkyls include Ethyl Corporation in St. Louis, Missouri and Texas Alkyls in Deer Park, Texas.[29] Both of these facilities were using benzene as of 1984.[29] However, no specific emission factors were found for these

TABLE 34. INDUSTRIES AND PRODUCTS POSSIBLY USING BENZENE AS A SOLVENT[13,14,29]

Rubber tires[a]
Miscellaneous rubber products[a]
Adhesives manufacture[a]
Gravure printing inks[a]
Printing and publishing[a]
Trade and industrial paints[a]
Paint removers[a]
Synthetic rubber[a]
Floor coverings[a]
Laboratories
Degreasing of metal furniture, primary metals
Pharmaceuticals manufacture
Alcohols production
Miscellaneous small volume chemicals
General organic synthesis
Textiles

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[a] A previous report, cited in Reference 29, indicated that benzene use in these categories has been discontinued.

TABLE 35. UNITED STATES PRODUCERS OF ETHANOL OR ISOPROPANOL[11]

Facility[a]	Location	Annual Capacity (10^6 Gallons)
ETHANOL		
American Development Corporation	Hamburg, IA Hastings, NE	15
American Fuel Technologies, Inc.	Federalsburg, MD	45
Archer Daniels Midland Company ADM Processing Division	Cedar Rapids, IA Decatur, IL Peoria, IL	500
Dawn Enterprises	Walhalla, ND	10
Eastman Kodak Company Eastman Chemical Products, Inc., subsidiary Texas Eastman Company	Longview, TX	25
Energy Fuels Development Corporation	Portales, NM	10
Georgia-Pacific Corporation Chemical Division	Bellingham, WA	6
Grain Processing Corporation	Muscatine, IA	60
High Plains Corporation	Colwich, KS	10
Kentucky Agricultural Energy Corporation	Franklin, KY	21
Midwest Grain Products, Inc.	Atchison, KS Pekin, IL	22 19
National Distillers and Chemical Corporation Chemicals Division U.S. Industrial Chemicals Company, division	Tuscola, IL	66
New Energy Company of Indiana	South Bend, IN	52
Pekin Energy Company	Pekin, IL	60
Shepherd Oil, Inc.	Jennings, LA	35
South Point Ethanol	South Point, OH	60

TABLE 35. UNITED STATES PRODUCERS OF ETHANOL OR ISOPROPANOL[11] (Continued)

Facility[a]	Location	Annual Capacity (10^6 Gallons)
A. E. Staley Manufacturing Company Special Products Group Ethanol Division	Loudon, TN	40
Tennoll Energy, Inc.	Jasper, TN	26
Union Carbide	Texas City, TX	120
Universal Foods Corporation	Juneau, WI	10
TOTAL ETHANOL		1214
ISOPROPANOL		
Atlantic Richfield Company	Channelview, TX	50
Exxon Corporation	Baton Rouge, LA	835
Shell Oil Company	Deer Park, TX Wood River, IL	600 340
Union Carbide	Texas City, TX	700
TOTAL ISOPROPANOL		2525

[a] The following companies have the facilities to produce ethyl alcohol, primarily for fuel use, in quantities of 10 million gal/year or less (except as noted): Alcohol Energy Corporation - Staley, NC; Baca Food and Fuel Cooperative - Campo, CO; Bornhoft, Paul - Merino, CO; A. Smith Bowman Distillery Corporation - Reston, VA; Charmel Energy Company - Muleshoe, TX; Coburn Enterprises, Inc. - Sherman, SD; Colorado Gasohol, Inc. - Walsh, CO; Crystal Fuel, Inc. - Bonaparte, IA; Ecological Energy, Inc. - Roca, NE; Food and Energy, Inc. - Litchfield, MA; Lenox Grain Fuels, Inc. - Lenox, IA; Marlin Car Care - Marlin, TX; A. E. Montana, Inc. - Amsterdam, MT; Raven Alcohol Distillery - Selma, CA; Southern Distilleries Company - Ashford, AL; Spudcohol - Pingree, ID; Syncorp, Inc. - Roberta, GA; U.S. Gasohol Corporation - Lockeford, CA; White Flame Fuels, Inc. - Van Buren, AR

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities and processes used by consulting current listings and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. These data on producers and locations are as of January 1987.

sources. A report from Texas Alkyls indicated that of the 490,000 pounds of benzene purchased, about 100 pounds would be lost to the atmosphere as fugitive emissions from tank truck off-loading and laboratory activities.[29]

BENZENE EMISSIONS FOR TREATMENT, STORAGE, AND DISPOSAL FACILITIES (TSDF)

Benzene may be emitted from treatment storage and disposal facilities (TSDF) and domestic refuse sites, depending on the types of waste handled or disposed. For example, in one recent study of landfill gas from municipal and industrial disposal sites in England, benzene was detected in all eight sites investigated.[31] This study sampled the landfill gas in situ and ambient measurements were not taken. However, it seems likely that benzene may be emitted from landfills.

No emission factor for benzene may be estimated for landfills or TSDF because the quantity of emissions depends on waste type and disposal techniques. The reader is urged to investigate specific sites to determine the potential for benzene emissions from these sources. Reference 32 documents some analytical results showing benzene concentrations of municipal landfill gas.

BENZENE EMISSIONS FROM STATIONARY COMBUSTION SOURCES

Benzene may be emitted from stationary combustion sources such as external combustion boilers, hazardous waste incinerators, hospital waste incinerators, and ferrous metallurgical furnaces.[32,33,34,35] Few data are available quantifying these benzene emissions. The data located during this research effort are discussed below.

Small amounts of hydrocarbons, including benzene, are produced and emitted during coal, oil, and gas combustion. More hydrocarbons are produced and emitted if a combustion unit is not properly operated and maintained. No specific emission factors were discovered for benzene emissions from external combustion boilers. However, one reference reported that the exhaust stream from a natural gas-fired boiler contained 1.18 percent by volume (or 4 percent by weight) benzene.[32] The same reference reported benzene content of 0.42 percent by volume (1.90 percent by weight) for emission stream from a coke oven gas boiler.[32] (See also Appendix B.)

Benzene has also been identified in air emissions from hazardous waste incinerators.[34] In a series of comprehensive tests of hazardous waste incinerators, benzene was frequently observed in the emission/exhaust streams (along with toluene, chloroform, naphthalene, and tetrachloroethylene). Several reasons were suggested to explain the prevalence of benzene (and the other compounds) in the emissions. First, the destruction efficiency for the compounds could be poor, given the low concentrations of the compounds in the waste feed. Second, the compounds could be input from sources other than the waste feed. Finally, the compounds could be actual products of some combustion reactions.[34] None of the likely reasons was especially favored over the others in the referenced report. Also, no actual emission factors were given in the report. The reported benzene content of the stack effluent ranged from 12-670 ng/l.[34]

Few data are available describing the emissions of benzene (or other compounds) from hospital refuse incinerators. One test report, conducted by the California Air Resources Board, showed mass emission rates of 0.1-0.4 lb/hour benzene.[35] The dual chamber incinerator had an average feed rate of 783 lb refuse/hour during the test. Feed consisted of 10 percent moisture, 30 percent plastic, 65 percent paper, and 5 percent other material.

Metallurgical furnaces are another type of stationary combustion source that are sources of benzene emissions.[32,36] For example, organic compounds have been identified as potential in emissions from iron and steel manufacturing sources. Possible sources of the organics include fuel combustion, the presence of organics on scrap metals, and use of organic binders for pellets and agglomerates. At foundries, organics may be emitted because they are present in core binders and additives, coating oils, lubes, and paints.[36] The organic emissions are reported to contain benzene.[33] While no emission factors specifically for benzene emissions from metallurgical operations were found, one reference contained emission factors for organics from the iron and steel industry, iron foundry industry, and ferroalloy industry. These emission factors are summarized in Table 36. Some speciation data are available to help determine what fraction of the organic emissions may be benzene. For example, one reference (see Appendix B) indicates that for a gray iron foundry, exhaust gases from 12 binder systems and sand formulations during pouring/casting operations contained 34.7 percent benzene by weight.[33] No other more specific emission factors for benzene were found for metallurgical furnaces.

Sewage sludge incineration is another potential source of benzene emissions. In a series of tests using the volatile organic sampling train (VOST), benzene was detected in stack gases at concentrations of 5 to 31 ug/dscm.[37] No specific emission factors were found for benzene emissions from sewage sludge incineration.

TABLE 36. SUMMARY OF ORGANIC EMISSION FACTORS FOR THE IRON AND STEEL, IRON FOUNDRY, AND FERROALLOY INDUSTRIES[36]

	Normalized Organic Emission Factor (lb/ton)[a]
Iron and Steel Industry	
By-product Cokemaking	3.90
Blast Furnace Ironmaking	1.17
Sinter Production	3.20
Basic Oxygen Process Steelmaking	0.0018
Electric Arc Furnace Steelmaking	0.0995
Open Hearth Furnace Steelmaking	0.0188
Hot Forming and Finishing Operations	0.184
Iron Foundry Industry	
Cupola Furnace Melting	0.195
Electric Arc Furnace Melting	0.160
Inoculation	0.0013
Metal Pouring and Cooling	0.209
Casting Shakeout	1.89
Ferroalloy Industry	
Open Submerged Arc Furnace Smelting	
Silicon Metal Alloys	10.2
Ferrosilicon Alloys	1.86
Ferromanganese Alloys	0.340
Ferrochromium Alloys	0.645
Covered Submerged Arc Furnace Smelting	
Ferrosilicon Alloys	0.225
Ferromanganese Alloys	0.0479
Ferrochromium Alloys	0.0614

[a] Emission factors normalized to lb/ton finished product (i.e., total steel products, net castings, total ferroalloys).

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SECTION 6

SAMPLING AND ANALYTICAL METHODS

The procedures presented in this section are methods that have been published by the U. S. Environmental Protection Agency (EPA) as viable methods for the sampling and analysis of volatile organic compounds (VOCs) from fugitive and industrial process sources. The analytical schemes have been modified to allow the detection of benzene at low levels (1 part per million, ppm, or less) with good precision and reproducibility. The sampling and analytical procedures for each recommended method are summarized together in this section. These methods are EPA Reference Method 21, EPA Reference Method 18, and the "Protocol for the Collection and Analysis of Volatile Principal Organic Hazardous Constituents (POHCs) Using the Volatile Organic Sampling Train (VOST)."

EPA Reference Method 21 - Determination of Volatile Organic Compound Leaks[1] is the method to use to detect the presence of fugitive emissions of benzene and other volatile organic compounds. This method applies to leaks from process equipment such as valves, flanges, connections, pumps, compressors, pressure relief valves, pumps and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals. Method 21 cannot be used to quantitate volatile organic compound leaks from these sources.

EPA Reference Method 18 - Measurement of Gaseous Organic Compound Emissions by Gas Chromatography describes the sampling and analytical procedures that are recommended for quantifying benzene in gaseous process streams.[2] The procedures published in this method have been used to permit quantification of benzene from fugitive sources.[3] They can also be used to sample and analyze benzene in ambient air.

The detection limit for the procedures in Method 18 is determined by the detector and column utilized for analysis but is about 1 ppm. The upper limit may be extended past the detector and column limits by sample dilution or by using a smaller gas sampling loop.

In general, direct interface sampling, dilution interface sampling, integrated sampling using evacuated containers with Tedlar or aluminized Mylar bags, or sampling onto adsorption tubes filled with activated charcoal are the methods that are recommended in Method 18 for sampling benzene emissions. The components of the sample are analyzed with a gas chromatograph and measured using a suitable detector. The eluted compounds are identified and quantified by comparing elution times and peak heights with those of known standards.

An alternative to monitoring for benzene emissions by Method 18 is the "Protocol for the Collection and Analysis of Volatile POHCs Using VOST."[4] This method was recently developed by EPA's Office of Research and Development to determine the destruction and removal efficiency of volatile POHCs from the stack gas effluents of hazardous waste incinerators. Volatile POHCs are those POHCs with boiling points between 30° and 100°C. The analytical portion of this procedure is very similar to the procedure described in EPA Reference Method 602 - Purgeable Aromatics which requires thermal desorption of the sample onto an analytical trap.[5]

The EPA Urban Air Toxics Monitoring Program is a national ambient air screening study, sponsored by EPA, to help State and local agencies address the magnitude of the air toxics problem in urban areas. Three types of samples are collected under the program. One type is collected using stainless steel canisters. This method is appropriate for VOC, including benzene. The canister method is described in this section.

SAMPLING AND ANALYTICAL PROCEDURES

Reference Method 21 - Determination of Volatile Organic Compound Leaks

A portable volatile organic compound (VOC) instrument detector capable of measuring benzene concentrations less than 10,000 ppmv is used to determine whether there are fugitive emissions or no detectable emissions. Some detection methods that are acceptable are catalytic oxidation, flame ionization, infrared absorption, and photoionization.

The precision and accuracy of this method are dependent on the compounds that are to be identified and the detection instrument that is chosen. Due to the nonlinear response of benzene around 10,000 ppmv, this technique cannot be used to quantitatively determine fugitive VOC emissions or to predict mass emission rates from fugitive sources.

An approach used in the past to predict mass emissions due to industrial fugitive sources has been equipment inventories. This involved physically enclosing all fugitive sources within a plant with an inert bag and measuring the emissions to determine the levels of and frequency of occurrence.[6]

As an alternative to an equipment inventory, a fenceline measurement technique can be used to quantitate fugitive emission concentrations at ground level outside of a plant.[3] A study was conducted outside of a maleic anhydride plant utilizing the Method 18 integrated bag sampling technique described later in this section.

Ambient air samples were collected from strategic locations around the plant. Care was taken when choosing the sampling locations so that the background concentration of benzene in the air could be differentiated from the concentrations attributed to fugitive and source emissions. Benzene analysis was conducted using a gas chromatograph (GC) equipped with a flame ionization detector and a 10 ft. x 1/8 in. column of 10 percent SP-2100/0.1 percent Carbowax on 100/120 mesh Supelcoport.

Modeling predictions were compared to the test data results to confirm the sources of emissions. This ambient monitoring study concluded that the approach utilized in this technique may be accurate enough to predict actual benzene fugitive emissions from industrial sources.

Reference Method 18 - Measurement of Gaseous Organic Compound Emissions by Gas Chromatography

A field site presurvey is initially conducted to obtain all the information necessary to design an emission test. Presurvey data include, but are not limited to, the average stack temperature and range, static pressure, and the particulate and moisture concentrations in the stack effluent. In addition, presurvey samples are collected to identify and approximate the concentration of benzene and other components in the effluent. When this information is known, the most appropriate sampling and analytical scheme to use can be determined.

The prescribed sampling protocol requires that the entire sampling train be leak free throughout the entire source testing process. Precautions to eliminate interferences from particulate matter, moisture condensation, and contamination need to be included in the sampling protocol.

There are basically four procedures that may be utilized to sample and analyze benzene from stack effluents. The correct procedure to use is dependent on the source conditions.

Direct Interface Sampling and Analytical Procedure--

This procedure can be utilized for determining benzene concentrations from sources with temperatures less than 100°C. This procedure requires that the analyte concentration is not so great as to saturate the detector and that the moisture content of the gas does not interfere with the analysis. A calibration standard or sample is heated to 3°C above the source temperature and pumped through a sample line to a GC. The instrument should include a Flame Ionization Detector (FID), column, temperature controlled loop and valve assembly, and temperature programmable oven. A schematic diagram of the direct interface sampling system is shown in Figure 27.

The appropriate column to use would be one that yields rapid and complete elution of benzene. The National Institute for Occupational Safety and Health (NIOSH) recommends using a glass, 3.0 m x 2 mm column, 10 percent OV-275 on 100/120 mesh Chromosorb W-AW, or equivalent.[7] This column will prevent interference by alkanes, but if interference by other volatile organic solvents is suspected, a less polar column is recommended. Optimum chromatographic conditions can be determined with calibration gas standards by varying the temperature program and/or the flow rate through the column.

Once a calibration curve has been established and optimum operating conditions are known, the samples can be analyzed using the same conditions as those used when analyzing the calibration gas mixture. Thorough flushing of the sample loop with the sample prior to analysis is necessary to eliminate crossover between standards and samples. Analysis is repeated until two consecutive analysis peak areas agree to within 5 percent of their mean value.

Dilution Interface Sampling and Analytical Procedure--

Some source samples may contain relatively high concentrations of benzene or other volatile organics which may overload the detector during analysis. A dilution interface sampling and analysis procedure allows for either a 10:1 or 100:1 dilution of the stack gas prior to detection.

The dilution interface sampling procedure is similar to the direct interface procedure. It requires a dilution system consisting of three pumps, three-way valves and connections contained in a box capable of heating to 120°C. The heated box is placed in line between the heated probe

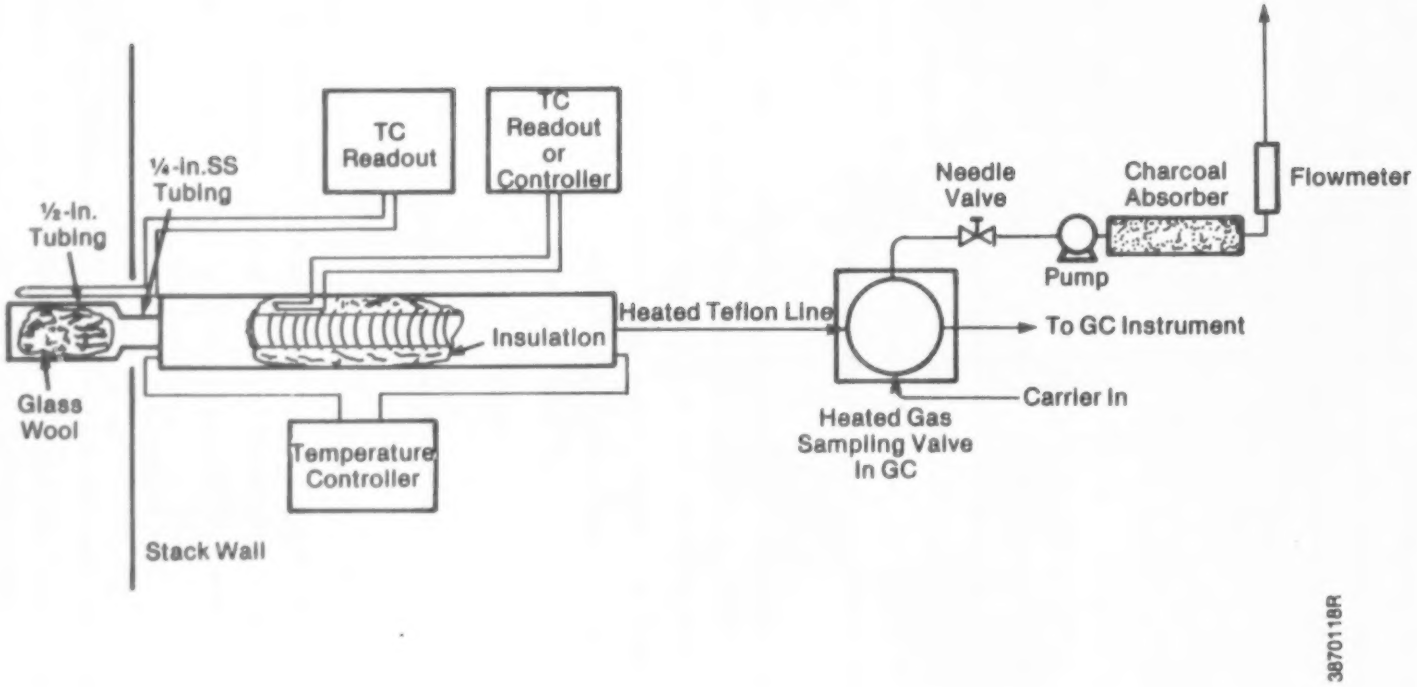
½-in.
Tubing
Glass
Wool
¼-in.SS
Tubing
Stack Wall
TC
Readout
TC
Readout
or
Controller
Temperature
Controller
Insulation
Heated Teflon Line
Heated Gas
Sampling Valve
In GC
Needle
Valve
Pump
Charcoal
Absorber
Flowmeter
To GC Instrument
Carrier In
3870118R

Figure 27. Schematic Diagram of the Direct Interface Sampling System[2]

and the heated gas sampling valve in the gas chromatograph. The temperature of the system is set to 3°C above the source temperature. A schematic diagram of the heated box required for the dilution interface sampling procedure is shown in Figure 28.

The analytical procedure for samples taken by using the dilution interface procedure is similar to that when using the direct interface procedure. The proper operation of the dilution system is proven by analyzing high level standards that are split through the 10:1 and 100:1 dilution stages. Data from the diluted standards must agree within 10 percent of the known values. Samples must be analyzed using the same chromatographic conditions and dilution ratios as the calibration mixture. Analysis is repeated until two consecutive analysis peak areas agree to within 5 percent of their mean value.

The Integrated Bag Sampling and Analytical Procedure

The integrated bag sampling technique collects samples by pulling stack gas into a prepurged evacuated bag, which is encased in a rigid container, at a rate proportional to the stack velocity. A diaphram-type pump, capable of delivering at least 1.0 L/minute, and a needle valve connected by a vacuum line to the bag container are in line prior to a flow meter. If samples contain high concentrations of organic materials, a dilution interface system used in conjunction with the integrated bag sampling procedure will prevent instrument detector saturation.

Variations of the integrated bag sampling procedure are:

1. the direct pump bag sampling procedure, and
2. the explosion risk area bag sampling procedure.

The first procedure places the pump and needle valve between the probe and bag, while the latter replaces the pump with another evacuated can. Figures 29 and 30 are schematic diagrams that show these modifications to

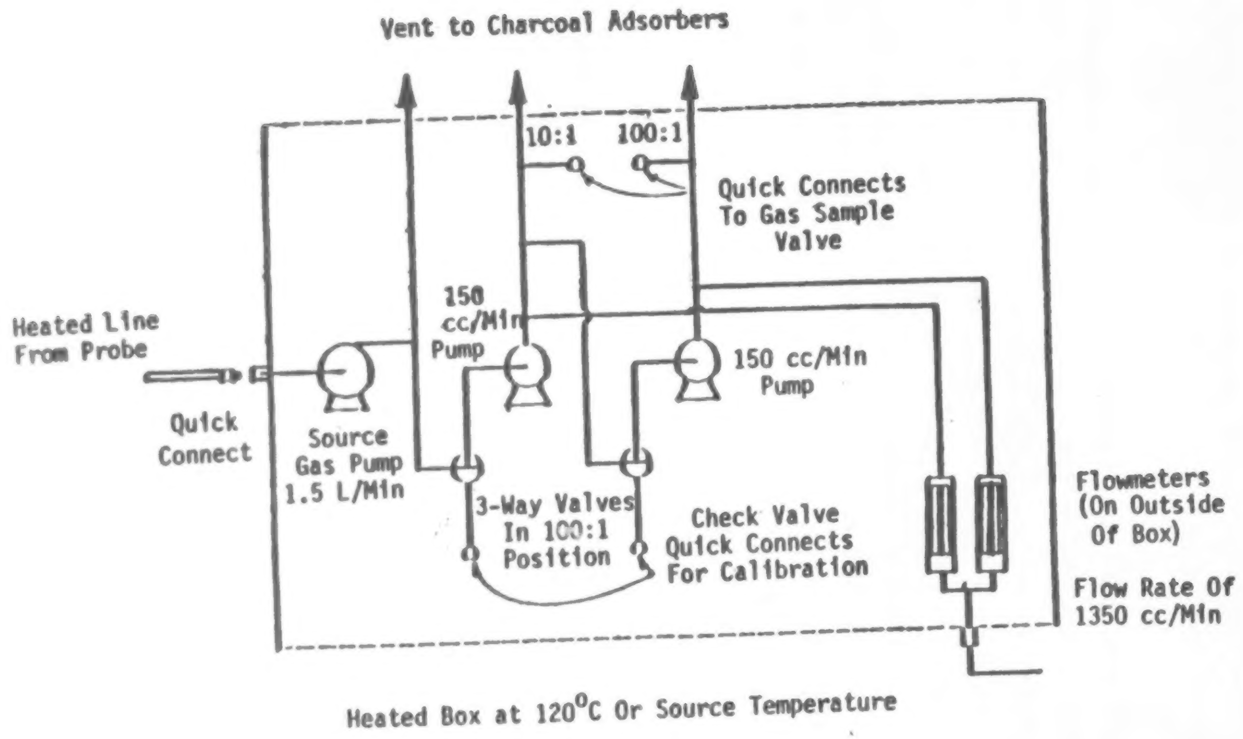
Vent to Charcoal Adsorbers
10:1
100:1
Quick Connects To Gas Sample Valve
Heated Line From Probe
Quick Connect
Source Gas Pump 1.5 L/Min
150 cc/Min Pump
150 cc/Min Pump
3-Way Valves In 100:1 Position
Check Valve Quick Connects For Calibration
Flowmeters (On Outside Of Box)
Flow Rate Of 1350 cc/Min
Heated Box at 120°C Or Source Temperature

Figure 28. Schematic Diagram of the Heated Box Required for the Dilution Interface Sampling Procedure[2]

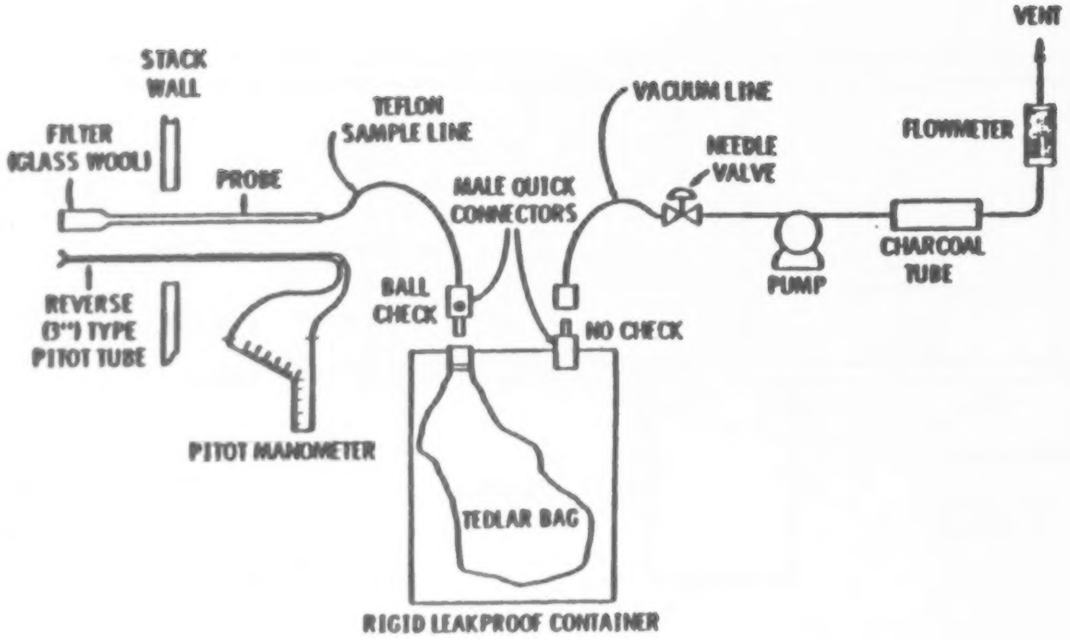
VENT
STACK WALL
FILTER (GLASS WOOL)
PROBE
TEFLON SAMPLE LINE
VACUUM LINE
NEEDLE VALVE
FLOWMETER
MALE QUICK CONNECTORS
PUMP
CHARCOAL TUBE
BALL CHECK
NO CHECK
REVERSE (3") TYPE PITOT TUBE
PITOT MANOMETER
TEDLAR BAG
RIGID LEAKPROOF CONTAINER

Figure 29. Schematic Diagram of the Intergrated Bag Sampling System[2]

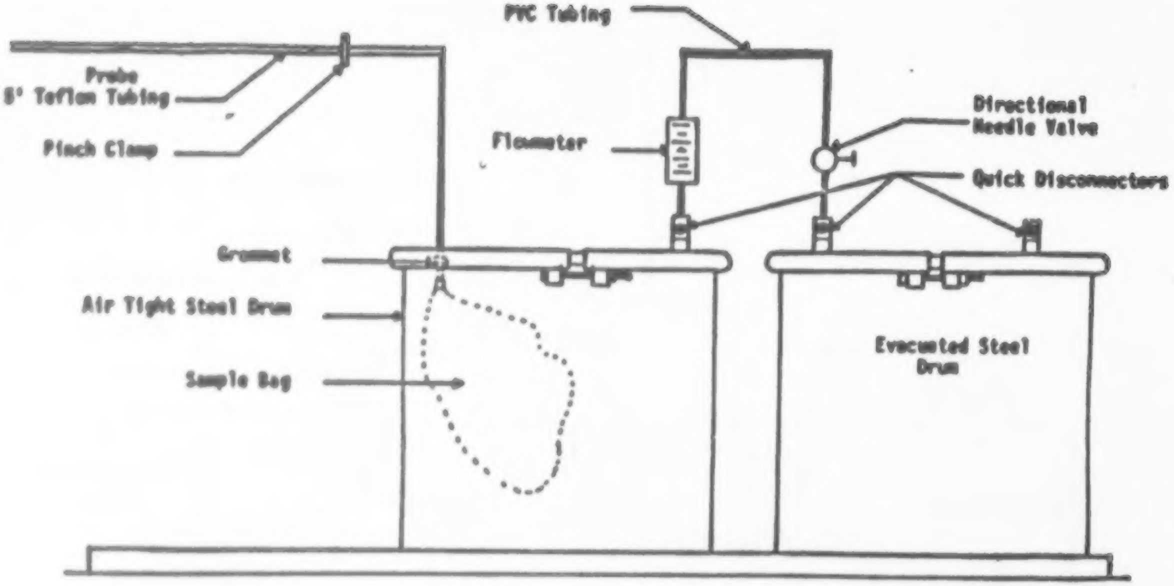
PVC Tubing
Probe
5' Teflon Tubing
Pinch Clamp
Flowmeter
Directional
Needle Valve
Quick Disconnectors
Grommet
Air Tight Steel Drum
Sample Bag
Evacuated Steel
Drum

Figure 30. Schematic Diagram of the Explosion Risk Area Gas Sampling System[2]

the integrated bag sampling procedure. Other modified bag sampling procedures may be considered when condensation is formed in the bag during sampling and the direct method of sampling can not be used. By heating the rigid container and sample bag to the stack temperature during sampling, condensation in the sample will be eliminated provided that the sample remains at the source temperature until analysis and that the components of the bag and rigid container can withstand the heat. Tedlar bag seals decompose at temperatures greater than 105°C.[8] An alternate procedure is to partially fill the sample bag with a known amount of inert gas prior to sample introduction. A measured amount of sample is then added into the partially filled bag and appropriate dilution factors are developed.

The analytical procedure for samples taken by using any of the variations of the integrated bag sampling procedure is similar to that when using the direct interface procedure. The difference is that samples have up to two hours after sampling before analysis is required. This is an advantage which allows the analyst time for other tasks.

Another advantage to using the integrated bag sampling procedure is that it does not restrict the analytical instrumentation location to the vicinity of the source location.

Adsorption Tube Sampling and Analytical Procedure--

Another Method 18 procedure that is approved by EPA for the sampling and analysis of benzene is the NIOSH Method No. 1501, issued on February 15, 1984.[7] This method is applicable for sampling benzene concentrations between 0.09-0.35 mg benzene per 1.0 mL desorption volume. The major components of this train include absorption tubes, a personal sampling pump (0.01 to 1.0 L/min), and a gas chromatograph equipped with a FID, column, and integrator.

For the purposes of source sampling, the adsorption tubes contain 800 mg coconut charcoal in the primary tube and 200 mg coconut charcoal in the backup tube. An alternate adsorption medium is silica gel. Adsorption tubes containing silica gel have 1040 mg in the primary tube and 260 mg in the backup tube. Tenax GC resin has been used in the past but can yield false positive responses for benzene.[9] Desorption efficiency of the adsorption medium must be determined by using an internal standard in the expected sample concentration range.

A sample pump and limiting orifice flow rate are calibrated prior to sampling with an adsorption tube in line by using a bubble flow meter. During sampling, a rotometer verifies that the sample rate remains constant at $\leq$0.20 L/minute.

Sample analysis requires transferring the adsorption medium into front and back half vials, adding 1 mL of carbon disulfide eluent into each vial and allowing the sample to stand for 30 minutes with occasional agitation. Then, 5 uL of this solution are injected into a precalibrated gas chromatograph. Instrument calibration is conducted daily by the least squares method over the appropriate range. Sample collection efficiency is determined by analyzing the front and back tubes separately. If the backup portion contains more than 10 percent of the total loading, sample breakthrough has occurred and a larger sampling portion of adsorption material is required. If samples contain high concentrations of benzene, a dilution interface system used in conjunction with the adsorption tubes will reduce instrument overloading and sample breakthrough.

The principal interference in this method is water vapor. This can be eliminated by the use of silica gel in line prior to the adsorption medium. If more than one compound is detected in the gaseous emissions, relative adsorptive capacity information must be determined. If present, water vapor may reduce this capacity further.

Protocol for the Collection and Analysis of Volatile POHCs Using VOST

Effluent gas is sampled with a Volatile Organic Sampling Train (VOST). The gas is cooled to 20°C and pulled through sorbent cartridge pairs containing approximately 1.6 grams of Tenax GC resin in the first trap, and

Tenax GC resin followed by petroleum based charcoal (weight ratio 3:1) in the second trap. Twenty liters of sample are collected during the sampling period. This may require up to six pairs of cartridges for each sample. A schematic diagram of the VOST is shown in Figure 31.

Due to high levels of moisture associated with the types of effluent that this method was designed to sample, the recommended analysis protocol is by thermal desorption, purge and trap by gas chromatography/mass spectrometry (P-T-O, GC/MS).[10] The sorbent cartridges are spiked with an internal standard and thermally desorbed with nitrogen through 5 mL of organic-free water onto an analytical absorbant trap. The analytical trap is rapidly heated to 180°C into a temperature programmed gas chromatograph that separates the effluent components. Low resolution mass spectrometry detects the compounds and quantitates them based on the internal standard.

A laboratory audit was conducted at four laboratories to evaluate the combined accuracy and precision of the VOST method.[11] Three of the laboratories analyzed their samples using thermal desorption purge and trap and gas chromatography/spectrometry (GC/MS). The other laboratory analyzed their samples by photoionization detector/Hall detector. The results of this audit indicate that based on an 18 ppb benzene standard, the VOST procedure can yield precision between 16.3 ± 1.2 ppb and 23.7 ± 1.0 ppb (mean ± standard deviation). These results indicate an accuracy range of the VOST method of between -9.7 percent to 32.0 percent. The VOST method is not officially designated as an approved method by EPA.

Stainless Steel Canister Method - Urban Air Toxics Program[12]

Urban air toxics samples are collected in evacuated 6-liter SUMMA® polished canisters. SUMMA® polishing involves treating the canisters such that a pure chrome/nickel oxide is formed on the interior surface. Canister sampling for VOCs is an alternative to VOC collection on solid sorbents (e.g., Tenax). Many VOCs which cannot be collected on Tenax (due to high

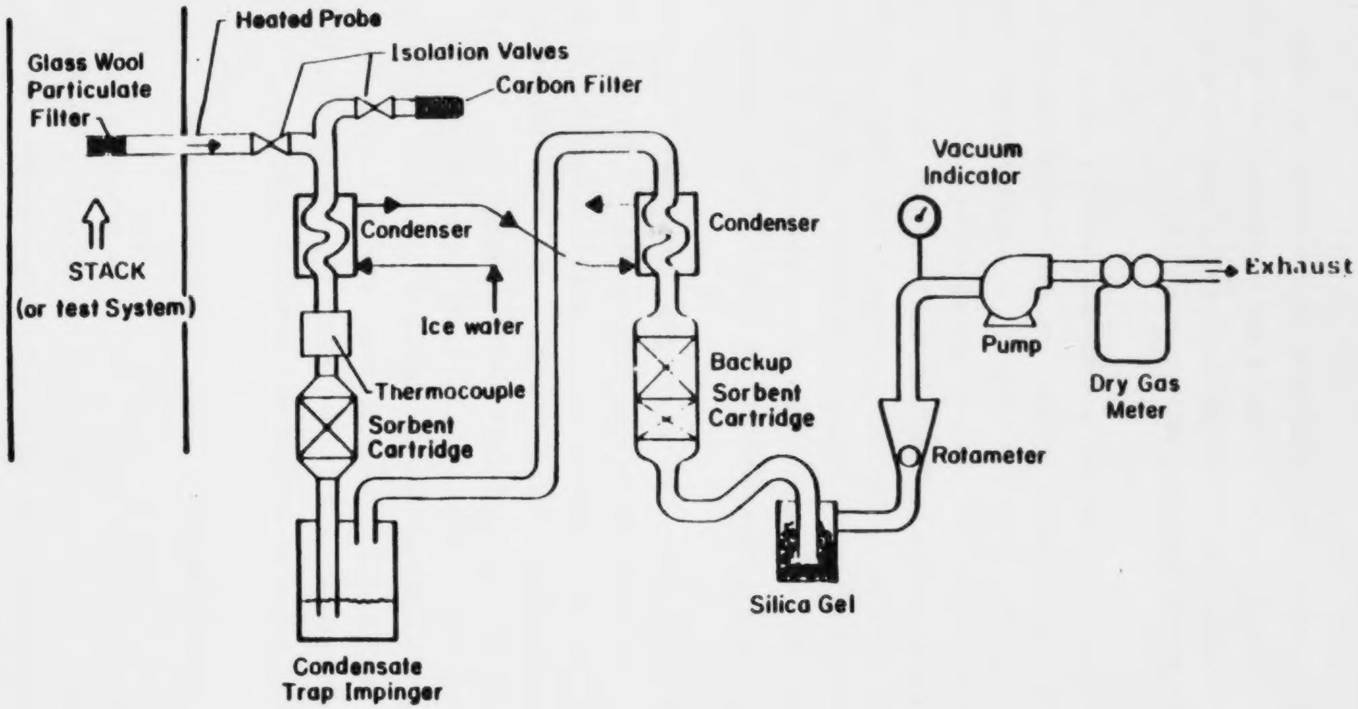
Heated Probe
Glass Wool Particulate Filter
Isolation Valves
Carbon Filter
STACK (or test System)
Condenser
Ice water
Thermocouple
Sorbent Cartridge
Condensate Trap Impinger
Condenser
Backup Sorbent Cartridge
Silica Gel
Vacuum Indicator
Rotameter
Pump
Dry Gas Meter
Exhaust

Figure 31. Schematic Diagram of the Volatile Organic Sampling Train[4]

volatility, polarity, or reactivity) can be efficiently collected and stored in canisters. Also, the canister contents may be analyzed repeatedly. The method is appropriate for benzene and is described in more detail below.

The evacuated canister method does not require a pump to collect a sample. Since the canister is at a pressure lower than atmospheric, the air sample flows through the heated manifold and mass flow controller and into the canister. The sampling assembly is shown in Figure 32. The electronic flow controller regulates and maintains a constant flow of approximately 3 cc/min to the canister. Prior to sample collection, a vacuum pump is activated by a timer to flush the heated manifold and particulate filter assembly with sample air. After a predetermined flushing period, a second timer opens the magnelatch solenoid valve to allow sample gas to enter the evacuated canister. After sample collection, the canisters are returned to a central laboratory for analysis of the ambient air samples. Collection of ambient air samples in canisters provides a number of advantages, including:

- convenient integration of ambient samples over a specific period,
- ability to ship and store samples,
- remote sampling capability with subsequent central laboratory analysis,
- unattended sample collection,
- analysis of samples from multiple sites with one analytical system, and
- collection of duplicate samples for assessment of sampling precision.

Sample Analysis

The air toxics samples are analyzed by a gas chromatograph equipped with photoionization, electron capture, and flame ionization detectors. For separation and subsequent identification by the selective detectors, the GC multi-detector technique relies on the analytes' retention times and selective detector peak response ratios for specific compounds such as benzene.

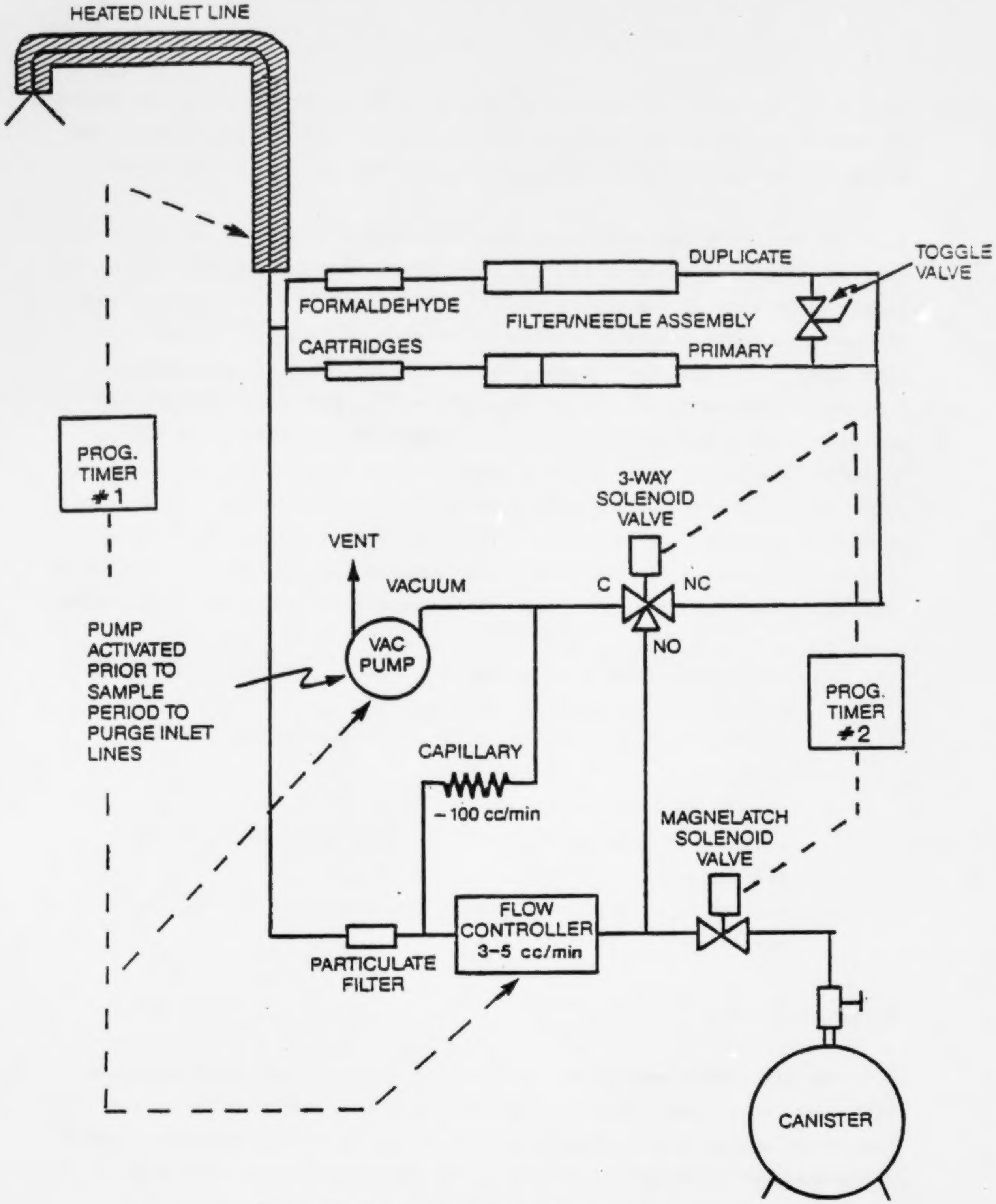
HEATED INLET LINE
DUPLICATE
TOGGLE VALVE
FORMALDEHYDE
FILTER/NEEDLE ASSEMBLY
CARTRIDGES
PRIMARY
PROG. TIMER #1
3-WAY SOLENOID VALVE
VENT
VACUUM
C
NC
NO
VAC PUMP
PUMP ACTIVATED PRIOR TO SAMPLE PERIOD TO PURGE INLET LINES
PROG. TIMER #2
CAPILLARY
~100 cc/min
MAGNELATCH SOLENOID VALVE
FLOW CONTROLLER 3-5 cc/min
PARTICULATE FILTER
CANISTER

Figure 32. Sampling Assembly for 24-Hour Urban Toxics Monitoring Program[12]

The analytical system consists of a cryogenic trap, a GC column, and selective detectors. In the cryogenic trap, the air toxics are concentrated prior to GC separation. The trap is then heated and the previously collected organic compounds volatilize and are carried to the GC column by the carrier gas. The GC column is temperature programmed for subambient cooling to provide improved resolution for the compounds of interest. After the column separates the organics, the effluent gas stream containing the separated organics enters a series of detectors consisting of electron capture, photoionization and flame ionization. The individual detectors respond to the sample components as a succession of peaks above a baseline on the chromatogram.

The area under the peak approximately quantifies the component, while the time lapse between injection and emergence of the peak serves as a preliminary identification. Detector peak response ratios are also used to perform peak identification. Further confirmation and identification will be performed on 20 percent of the total samples by gas chromatography/mass spectroscopy (GC/MS). Concentrations of toxic species are reported in units of ppb by volume (ppbv).

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APPENDIX A

DERIVATION OF EMISSION FACTORS

APPENDIX A
DERIVATION OF EMISSION FACTORS

A.1 BENZENE EMISSIONS FROM ETHYLENE PLANTS

The emission factor for other intermittent emissions (Vent E) in Table 23 were derived as follows.

Data from Reference 1 showed that, for a 453.5 Gg/year capacity ethylene plant with 50:50 naphthalene/gas oil feed, material lost as a result of compressor outages over the first 5 years of plant operation were:

	Total Material Lost (Mg) by Year of Operation					Average Over Five Years (Mg/Year)
	1	2	3	4	5	
Single train	9878	6857	5469	4653	3837	6138.7
Dual train	1224	857	735	612	490	783.6

On a per hour basis, the material lost from compressor outages in 700.8 kg/hr for single trains and 89.5 kg/hr for dual trains (assuming 8760 hr/year operation). Then, assuming that there is 5.85 percent benzene in the charge gas (Reference 1):

For single trains - 700.8 kg/hr x 0.0585 = 40.99 kg benzene/hr
For dual trains - 89.5 kg/hr x 0.0585 = 5.24 kg benzene/hr

Then the ratio of 453.5:544.2 (plant capacity) was applied to the emission rates for benzene to account for differences in material use and the emission rate in kg/hr was converted to g/Mg ethylene:

Single train - 40.99 x 1.2 (size ratio) x 16.1 (conversion to g/Mg) = 791.9
Dual train - 5.24 x 1.2 (size ratio) x 16.1 (conversion to g/Mg) = 101.1

For secondary emissions (emissions from wastewater handling and treatment), the emission factor was derived from estimates of the amount of wastewater produced per Gg ethylene, the average concentration of total organics in the wastewater, the estimated kg VOC emitted/kg wastewater, and the estimated benzene concentration in the emitted VOC. All data were taken from Reference 1.

For a 544 Gg/year plant:

2166 m^3 wastewater generated/Gg ethylene x 544 Gg ethylene = 1,178,304 m^3 wastewater or 1,178,304,000 kg wastewater per year or 134,510 kg/hr (based on 8,760 hr/year operation)

A VOC concentration in the wastewater of 104 ppm was used:

104 kg/10^6 kg = X kg/134,510 kg or 14 kg VOC/hr in wastewater

Then, assuming 25 percent of the VOC is emitted and, of that, 38.5 percent is benzene,

14 x 0.25 x 0.385 = 1.35 kg/hr or 21.7 g/Mg

A.2 DERIVATION OF EMISSION FACTORS FOR FUGITIVE EMISSIONS FROM CHLOROBENZENE PRODUCTION

Emission factors for fugitive benzene emissions from chlorobenzene manufacture were based on factors established for fugitive emissions at refineries.[2] According to the source of these data, preliminary test results suggest that fugitive emissions from refineries are comparable to those at chemical plants.[2] Thus, the factors for benzene in Table 24 are based on summation of the factors in Table A-1 and production capacity of 96 Gg/year. The hypothetical plant is estimated to have 102 pumps handling VOC, 22 of which handle benzene. The estimated number of valves is 792, 45 of which service benzene vapor and 173 service benzene liquid. The

TABLE A-1. FUGITIVE EMISSION FACTORS FOR PETROLEUM REFINERIES USED TO DEVELOP FACTORS FOR CHLOROBENZENE PRODUCTION

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump Seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline Valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/Relief Valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor Seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light-liquid means any liquid more volatile than kerosene.

estimated number of pressure relief valves is 12, 6 of which service benzene. The estimated number of flanges is 1848, of which 486 service benzene. The fugitive emission factors from Table A-1 were applied to this valve, pump, and flange count to determine the fugitive emissions shown in Table 24.[2]

The storage- and handling-emission calculations in Table 24 were based on fixed-roof tanks, half full, and a diurnal temperature variation of 11°C and with the use of the emission equations from AP-42.[2] However, breathing losses were divided by four to account for recent evidence indicating that the AP-42 breathing loss equation overestimates emissions.[2]

Breathing and working losses can be estimated from emission equations developed for EPA Publication No. AP-42 (Reference 3). The equations used in estimating emission rates from fixed-roof tanks are:

$$L_{total} = L_B + L_W$$

$$L_B = 1.02 \times 10^{-5}\, M_v \, {\frac{P}{14.7 - P}}^{0.68} D^{1.73}\, H^{0.51}\, T^{0.5}\, F_P C K_c \qquad (2\text{-}1)$$

$$L_W = 1.09 \times 10^{-8}\, M_v P V N K_n K_c \qquad (2\text{-}2)$$

Where:

L_T = total loss per tank (Mg/yr)
L_B = breathing loss per tank (Mg/yr)
L_W = working loss per tank (Mg/yr)
M_v = molecular weight of product vapor (lb/lb mole)
P = true vapor pressure of product (psia)
D = tank diameter (ft)
H = average vapor space height (ft); use an assumed value of one-half the tank height
T = average diurnal temperature change in °F; assume 20°F as typical value
F_p = paint factor (dimensionless)
C = tank diameter factor (dimensionless) for diameter equal to or >30 feet, $C = 1$

K_c = product factor (dimensionless) = 1.0 for volatile organic liquids (VOL)

V = tank capacity (bbl)

N = number of turnovers per year (dimensionless)

K_n = 1, for turnovers <36

Several assumptions were made in order to calculate emission factors on a per tank basis, for both breathing and working losses, from a typical fixed-roof tank storing gasoline. The following assumptions were used:

M_v = 66 lb/lb mole (for gasoline)
P = 5.2 psia (for gasoline)
D = 50 feet
H = 48/2 = 24 feet
T = 20°F
F_p = 1.0 (for a white tank)
C = 1.0
K_c = 1.0 (for VOL)

Therefore, after substituting into equation 2-1,

$$L_B = 1.02 \times 10^{-5} (66) {\frac{5.2}{14.7 - 5.2}}^{0.68} (50)^{1.73} (24)^{0.51} (20)^{0.5} (1)(1)(1)$$

$$= 8.8 \text{ Mg/yr}$$

Using equation 2-2 and these additional assumptions:

N = 13 turnovers per year
V = 16,750 bbl tank capacity

$$LW = 1.09 \times 10^{-8} (66) (5.2) (16{,}750) (13) (1) (1)$$
$$= 34.2 \text{ Mg/yr}$$

In summary, the VOC emission factors for a typical fixed-roof tank storing gasoline are 8.8 Mg/yr from breathing losses and 34.2 Mg/yr from working losses.

Standing-storage losses and withdrawal losses are the major sources of emissions from external floating-roof storage tanks. From the equations presented below, it is possible to estimate both the withdrawal loss and the standing-storage or roof seal loss from an external floating-roof tank. These equations are taken from Reference 3.

$$L_T = L_W + L_{SE}$$

$$L_W = 4.28 \times 10^{-4}\ QCW_L/D\ (1 + N_cF_c/D) \qquad (2\text{-}3)$$

$$L_{SE} = K_s\ V^n\ P^*DM_vK_c/2205 \qquad (2\text{-}4)$$

Where:

L_T = total loss (Mg/yr)

L_W = withdrawal loss (Mg/yr)

L_{SE} = standing-storage or seal loss (Mg/yr)

Q = product average throughput (bbl/yr)

C = product withdrawal shell clingage factor (bbl/10^3 ft^2)

D_c = zero for self-supporting floating-roof tanks

F_c = effective column diameter

W_L = density of product (lb/gal)

D = tank diameter (ft)

K_s = seal factor (dimensionless)

V = average windspeed (mph); 10 mph assumed average windspeed

N = seal windspeed exponent (dimensionless)

p^* = vapor pressure function (dimensionless)

M_v = molecular weight of product vapor (lb/lb mole)

K_c = product factor (dimensionless) = 1.0 for VOL

For the purposes of calculating the external floating-roof emission factors, several additional assumptions were made as follows:

Q = the value for product throughput varied from State to State (bbl/yr)

C = 0.0015 (for light rust)

W_L = 5.6 lb/gal (for gasoline)

K_S = 1.2 (for a metallic shoe with primary seal, assume welded tank) and 0.8 (for a metallic shoe with secondary shoe seal); 0.2 (for metallic shoe with rim mount secondary shoe seal)[2]

193

V = 10 mph

N = 1.5 (for a metallic shoe with primary seal) and 1.2 (for a metallic shoe with secondary seal)

$P^* = (P/P_A)/[1 + (1 - P/P_A)^{0.5}]^2$

Where: P_A = average atmospheric pressure = 14.7 psia

P = true vapor pressure at average actual organic liquid storage temperature = 5.6 psia

Therefore: $P^* = (5.6/14.7)/[1 + (1 - 5.6/14.7)^{0.5}]^2 = 0.10871$

Therefore, after substituting into equation 2-3 and 2-4:

$$L_W = 4.28 \times 10^{-4}\ Q\ (0.0015)\ (5.6)/78$$
$$= 36 \times 10^{-7}\ Q/78 \text{ Mg/yr}$$
$$L_S = (1.2)\ (10)^{1.5}\ (0.10871)\ (78)\ (66)\ (1)/2205$$
$$= 9.6 \text{ Mg/yr for a metallic shoe with primary seal}$$
$$L_S = (0.8)\ (10)^{1.2}\ (0.10871)\ (78)\ (66)\ (1)/2205$$
$$= 3.2 \text{ Mg/yr for a metallic shoe with primary seal}$$

In summary, the VOC emission factors for a typical external floating-roof tank storing gasoline are 36×10^{-7} Q/78 Mg/yr from withdrawal losses, 9.6 Mg/yr from storage or seal losses on a tank with a metallic shoe primary seal and 3.2 Mg/yr from storage or seal losses on a tank with a metallic shoe secondary seal.

A.3 DERIVATION OF BENZENE EMISSION FACTOR FOR EXHAUST EMISSION OF LIGHT DUTY AND HEAVY DUTY TRUCKS

Reference 4 provided the following derivation of emission factors for benzene from truck exhaust:

Light duty trucks: $\frac{3.4\text{ g hydrocarbon}}{\text{mile}} \times 1.17\%\ \text{benzene in gasoline} \times 0.45 = 0.02\ \text{g/mile}$

Heavy duty trucks: $\frac{13.6\text{ g hydrocarbon}}{\text{mile}} \times 1.17\%\ \text{benzene in gasoline} \times 0.45 = 0.07\ \text{g/mile}$

The factor of 0.45 converts from v/v percent of benzene in the gasoline liquid to the w/w percent benzene in the vapor.

A.4 BENZENE EMISSIONS FOR VARIOUS VEHICLE TEST TYPES AND CONTROL TECHNOLOGIES

Table A-2 lists observed benzene emissions and hydrocarbon emissions for a series of tests on vehicles equipped with different control technologies.[5]

TABLE A-2. BENZENE EMISSIONS FOR DIFFERENT EXHAUST EMISSION CONTROL TECHNOLOGIES[5]

	N	HC (g/mile)	% Benzene	Benzene Emissions (mg/mile)
CUE (Crowded Urban Expressway)				
No Cat/Air	3	1.173	2.42	31.1
Oxid. Cat/No Air	12	1.360	4.11	54.7
Oxid. Cat/Air	10	0.892	3.42	30.0
Dual-Bed Cat/Air	12	0.414	3.83	16.4
*3-Way Cat/No Air	3	0.160	4.88	9.4
Federal Test Procedures				
No Cat/Air	3	2.233	2.33	52.3
Oxid. Cat/No Air	12	1.960	3.26	61.9
Oxid. Cat/Air	10	1.626	2.81	45.1
Dual-Bed Cat/Air	12	0.603	2.63	16.6
*3-Way Cat/No Air	3	0.350	4.16	14.7
NYCC (New York City Cycle)				
No Cat/Air	3	7.897	1.81	150.0
Oxid. Cat/No Air	12	6.092	3.03	170.4
Oxid. Cat/Air	10	6.013	2.23	148.3
Dual-Bed Cat/Air	12	2.447	2.14	56.3
*3-Way Cat/No Air	3	1.390	2.92	40.6

*Single-bed
Cat = catalyst
N = sample size

REFERENCES FOR APPENDIX A

1. U. S. Environmental Protection Agency. Organic Chemical Manufacturing. Volume 9: Selected Processes. Report 3. Ethylene. EPA-450/3-80-028d. Research Triangle Park, NC. 1980.

2. U. S. Environmental Protection Agency. Organic Chemical Manufacturing. Volume 6: Selected Processes. Report 1. EPA-450/3-80-028a. Research Triangle Park, NC. 1980.

3. U. S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors. Fourth Edition (Including Supplements 1-15 and Updates). Publication No. AP-42. Research Triangle Park, NC. 1985.

4. U. S. Environmental Protection Agency. Materials Balance for Benzene Level II. EPA-560/13-80-009. Washington, D.C. 1980. pp. 2-6 - 2-34.

5. Klausmeir, R., P. Anderson, and K. Wert. Evaluation of Mobile Source Control Strategies for Benzene. Prepared for the Western Oil and Gas Association. Radian Corporation DCN No. 85-245-024-01. Austin, TX. 1985.

APPENDIX B

DATA ON POTENTIAL SOURCES OF BENZENE FROM THE AIR EMISSIONS SPECIES MANUAL (DRAFT REPORT)

APPENDIX B

DATA ON POTENTIAL SOURCES OF BENZENE FROM THE AIR EMISSIONS SPECIES MANUAL (DRAFT REPORT)

The Pollutant Characterization Section, Noncriteria Pollutant Programs Branch of the U. S. Environmental Protection Agency is preparing a document that will assist in determining the composition of many emission streams from a variety of sources.[1] The data in that document are arranged in profiles containing the source type, control device, pollutant, CAS number, and weight percents of emission stream components. To provide the most data available about potential sources of benzene, the most recent species profiles from the draft report were reviewed and summarized.

Table B-1 shows the source descriptions, source classification code (SCC), indication of data quality, and percent (weight) of the emission that is benzene. The actual species profiles (and appropriate references cited in the profiles) should be checked before applying any of the profile data.

These profiles are presented to provide a means to estimate benzene emissions when a benzene-specific emission factor has not been established. For example, if the total VOC emissions for aircraft landings/takeoff are known, then the species data showing 1.79 weight percent benzene would be applied to the total VOC emissions to obtain an estimate of benzene emissions.

The species profile data are provided to supplement the emission factors in the main body of the report. The emission factors in the text were obtained from published literature and, in some cases, may be more process-specific than the factors obtained using the VOC species data in Table B-1. Before applying the emission factors on the species profiles, the reader is encouraged to review the references for both types of data to discern any peculiarities concerning the derivation of the data.

Contact the Pollutant Characterization Section, Noncriteria Pollutant Programs Branch, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, for more information about the benzene data summarized here, or for more information on the VOC species profiles.

TABLE B-1. POTENTIAL SOURCES OF BENZENE EMISSIONS AND APPROXIMATE BENZENE COMPOSITION OF THE EMISSIONS[a]

SCC	Source Description	Weight Percent Benzene	Profile Data Quality
3-03-009-01	Open Hearth Furnace with Oxygen Lance - ESP Control	13.60	C
4-02-999-99	Flavorseal Citrus Coating Wax - Uncontrolled Surface Coating	3.11	A
1-02-007-07 3-90-007-02	External Combustion Boiler Burning Coke Oven Gas - Uncontrolled	1.90	B
2-02-004-01 2-04-004-02	Reciprocating Diesel Fuel Engine - Uncontrolled	7.90	C
2-01-001-02 2-02-001-02 2-03-001-01	Reciprocating Distillate Oil Engine - Uncontrolled	7.90	D
3-03-003-02 3-03-003-03 3-03-003-05 3-03-003-06	By-product Coke Oven Stack Gas - Uncontrolled	14.10	C
3-05-001-04	Asphalt Roofing Tar Kettle - Uncontrolled	0.80	C
3-05-002-02	Asphaltic Concrete - In Place Road Asphalt - Uncontrolled	9.50	B
3-06-005-03 3-06-005-04	Refinery Fugitives - Covered Drainage/ Separation Pits - Uncontrolled	2.40	C
---	Solvent Use - General Pesticides - Uncontrolled	12.30	C
5-01-001-01 5-01-001-02	Bar Screen Waste Incinerator - Uncontrolled	7.70	D
3-90-007-01	Coke Oven Blast Furnace Gas - Uncontrolled	43.00	B
3-01-026-20	Automotive Tires - Tuber Adhesive - Uncontrolled	2.80	C

200

TABLE B-1. POTENTIAL SOURCES OF BENZENE EMISSIONS AND APPROXIMATE BENZENE COMPOSITION OF THE EMISSIONS^a (Continued)

SCC	Source Description	Weight Percent Benzene	Profile Data Quality
3-01-026-20	Automotive Tires - Tuber Adhesive, White Sidewall - Uncontrolled	7.70	C
4-03-01-010 4-03-01-011 4-03-01-012 4-03-01-109	Fixed Roof Tank - Crude Oil Production	0.10	C
4-04-003-01 4-04-003-02	Fixed Roof Tank - Crude Oil Refinery - Uncontrolled	2.40	C
3-06-008-01	Pipe/Valve Flanges - Uncontrolled	0.10	C
3-06-008-03	Pump Seals - Composite - Uncontrolled	0.50	C
---	Off-road Gasoline Motor Vehicles	2.66	E
---	Vessels - Gasoline	2.66	E
3-10-88-801	Oil and Gas Production - Fugitives (Unclassified)	0.10	D
3-10-001-01	Oil and Gas Production - Fugitives - Valves/Fittings in Liquid Service	0.10	D
3-10-002-03	Oil and Gas Production - Fugitives - Valves/Fittings in Gas Service	0.10	D
4-02-002-01 4-02-002-10	Surface Coating Application - Water-based Paint - Uncontrolled	0.36	C
4-03-010-03	Evaporative Emissions - Summer-blend Gasoline - Uncontrolled	0.77	B
4-03-010-01	Evaporative Emissions - Winter-blend Gasoline - Uncontrolled	1.56	B
3-01-133-03	Acetic Anhydride Production, Distillation Column Vent - Uncontrolled	2.00	D

201

TABLE B-1. POTENTIAL SOURCES OF BENZENE EMISSIONS AND APPROXIMATE BENZENE COMPOSITION OF THE EMISSIONS[a] (Continued)

SCC	Source Description	Weight Percent Benzene	Profile Data Quality
3-01-156-06	Cumene Production, Cumene Distillation System Vent - Uncontrolled	38.49	C
3-01-158-22	Cyclohexanone/Cyclohexanol - Phenol Hydrogenation Process, Distillation Vent - Condenser	28.07	E
3-01-195-02 3-01-195-04	Nitrobenzene Production - Reactor Vent, Washer/Neutralizer Vent	99.71	E
3-01-197-45	Ethylene [illegible]ion, Compressor Lube Oil Vent	2.07	C
3-01-206-01	Styrene Production - General	23.28	D
3-01-206-02	Styrene Production - Benzene Recycle - Condenser	34.38	D
3-01-206-03	Styrene Production, Styrene Purification - Condenser	41.46	E
3-01-301-01	Chlorobenzene Tail Gas Scrubber - Scrubber	56.96	C
3-01-301-02	Chlorobenzene - Benzene Drying Distillation	95.04	D
3-01-301-06	Chlorobenzene - Vacuum System Vent - Steam Jet	19.62	C
3-01-301-08	Chlorobenzene - Dichlorobenzene Crystal Handling - Uncontrolled	0.11	E
---	Residential Wood Combustion	18.91	D
4-06-004-01 4-06-004-03	Gasoline Marketing (Refueling Cars) - Uncontrolled	1.00	C
---	Commercial Aircraft Landing/Takeoff - Uncontrolled	1.93	B

TABLE B-1. POTENTIAL SOURCES OF BENZENE EMISSIONS AND APPROXIMATE BENZENE COMPOSITION OF THE EMISSIONS[a] (Continued)

SCC	Source Description	Weight Percent Benzene	Profile Data Quality
---	General Aviation - Aircraft Landing/ Takeoff - Uncontrolled	1.79	C
---	Military Aircraft Landing/Takeoff	2.01	B
---	Light-duty Gasoline Vehicles - Exhaust/Evaporative - Catalyst	2.80	B
3-04-003-20	Secondary Metal Production, Gray Iron Foundries - Pouring/Casting (Exhaust Gases from Binder Systems and Sand Formulations)	34.70	B
2-01-002-02 2-02-002-02 2-02-002-04 2-03-002-01	Internal Combustion Engine - Reciprocating Engine	0.11	B
---	Industrial Incineration	1.49	E
3-01-900-99	Chemical Manufacturing - Flares	10.00	D
3-05-002-01	Asphaltic Concrete - Natural Gas-fired Rotary Dryer	4.00	D
1-01-006-01	External Combustion Boiler - Natural Gas-fired - Uncontrolled	4.00	B
---	Diesel Fuel - Light-duty, Heavy-duty, and Off-highway Vehicles	1.90	C

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[a] Based on data gathered as part of the effort to revise the Air Emissions Species Manual. Species profiles that showed benzene as a component of the total exhaust stream are summarized in this table. The speciation data profiles used were dated August 4, 1987. Profile data quality are defined as follows:

Data Quality A:	Data set based on a composite of several tests using analytical techniques such as GC/MS and can be considered representative of the total population.

203

TABLE B-1. POTENTIAL SOURCES OF BENZENE EMISSIONS AND APPROXIMATE BENZENE COMPOSITION OF THE EMISSIONS[a] (Continued)

Data Quality B:	Data set based on a composite of several tests using analytical techniques such as GC/MS and can be considered representative of a large percentage of the total population.
Data Quality C:	Data set based on a small number of tests using analytical techniques such as GC/MS and can be considered reasonably representative of the total population.
Data Quality D:	Data set based on a single source using analytical techniques such as GC/MS; or data set from number of sources where data are based on engineering calculations.
Data Quality E:	Data set(s) based on engineering judgement; data sets with no documentation provided; may not be considered representative of the total population.

Emission control devices are given in Table B-1 if they were included in the species profile data.

REFERENCES FOR APPENDIX B

1. U. S. Environmental Protection Agency. Air Emissions Species Manual. Volume I. Volatile Organic Compound (VOC) Species Profiles. Draft Report. Noncriteria Pollutant Programs Branch. Research Triangle Park, North Carolina. October 1987.